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Development of Materials for a Military Overgarment for Protection against CW Agents and Studies of New Fluorochemicals For Use as Finishes

Final Summary Report 22

CONTRACT NO. DA-19-129-QM-1631 (OI 5150)

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DEVELOPMENT OF MATERIALS FOR A MILITARY OVERGARMENT FOR PROTECTION AGAINST CW AGENTS AND STUDIES OF NEW FLUOROCHEMICALS FOR USE AS FINISHES.

Final Summary Report.

UNITED STATES ARMY NATICK LABORATORIES

Project 1203, Report 22

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Contract DA-19-129-QM-1631 (OI 5150)

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Southern Research Institute
Birmingham, Alabama
July 31, 1964
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FOREWORD

This report covers work done from June 15, 1960, to May 31, 1964, under Contract DA-19-129-QM-1631 (OI 5150). This report is divided into the following four parts:

Part I.	Development of an Expendable Military Field Overgarment with Protection Against Chemical Warfare Agents in Liquid Form
Part II.	Development of Materials for an Overgarment Providing Protection Against Liquid, Vapor, and Aerosol
Part III.	Development of Materials for an Overgarment Providing Protection Against Liquid and Vapor
Part IV.	Studies of Fluorocarbon Compounds

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ABSTRACT

This report covers the work done to develop materials for a military overgarment to provide protection against chemical warfare agents and to prepare fluorochemicals for use as finishes for the materials.

The initial objective of this project was to develop an inexpensive, lightweight, expendable overgarment that would provide protection against chemical warfare agents in liquid form and that was durable enough to be worn for 6 hours. A search of the literature and a survey of industry disclosed no woven fabrics, nonwoven fabrics, films, papers, or foams that appeared to be suitable for preparing an inexpensive, lightweight overgarment that had all of the desired properties. Papers appeared to offer the most promise for development as suitable material for the overgarment because they were cheap, lightweight, permeable to air and water vapor, and could be treated to provide resistance to liquid CW agents. Poor abrasion resistance, poor snag and tear resistance, poor flexibility; and in the case of reinforced papers, poor adhesion between the scrim and surface layers were the major deficiencies of the commercial papers. Therefore, studies were made to overcome these deficiencies.

An experimental paper made from 50% nylon and 50% wood pulp fibers, reinforced with nylon scrim and treated to increase abrasion resistance and to provide CW-agent resistance was the best material found for the lightweight, expendable overgarment. Field evaluations of two such scrim-reinforced papers produced on commercial equipment indicated that they had a service life under combat conditions of 3-4 days.

Work on the design of the overgarment was begun at Southern Research Institute, but was completed by International Latex Corporation under Subcontract D-7933. A one-piece coverall-type overgarment and a two-piece pajama-type overgarment design were approved by the Project Officer.

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ABSTRACT (continued)

The next phase of the program was directed toward the development of materials that would be durable enough for wear for 3 to 21 days and that would provide protection against chemical warfare agents in liquid, vapor, and aerosol forms. A three-layer system consisting of an outer layer of Quarpel-treated nylon-cotton woven fabric to provide liquid resistance, a middle layer of either a Dacron-glass paper or a glass-viscose-vinyon material (Liner E-18) to provide aerosol resistance, and an inner layer of rayon nonwoven fabric treated with a chloroamide-resin mixture to provide vapor resistance possessed most of the desired physical properties. Before studies of two-layer and one-layer systems with resistance to agents in the three physical states were completed, the requirement for protection against agents in aerosol form was dropped and efforts were directed to development of a material for overgarments to provide protection against chemical warfare agents in liquid and vapor forms.

In this third phase of the program, attempts were made initially to produce a single-layer material for overgarments that would provide protection against liquid and vapor chemical warfare agents by treating one side of base fabrics with a liquid repellent and the other side with a reactive or absorbtive material that would retain agents in vapor form. The results were not promising, and the major effort in this phase of the program was spent on the development of a two-layer system. The most promising two-layer system developed consisted of an outer layer of mercerized woven cotton fabric treated with Zepel B and an inner layer of a rayon nonwoven fabric or a polyurethane foam containing activated carbon with an acrylic latex as a binder. Several hundred yards each of scrim-reinforced nonwoven fabric and of polyurethane foam/nylon laminate were prepared and treated with the activated carbon/latex mixture on plant equipment. These materials were supplied to the U. S. Army Natick Laboratories for evaluation.

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ABSTRACT (continued)

The fourth phase of the program was concerned with the development of new and improved fluorocarbon compounds as finishes for overgarment materials to provide oil, water, and flame resistance. Eleven new fluorocarbon compounds were synthesized and screened as oil and water repellents for cellulose materials and two fluorocarbon compounds were synthesized and screened as combined oil- and water repellent and flame retardant. One of the chemicals, perfluorocaprylamidomethylpyridnium chloride, was found to provide good oil- and water-repellent properties and was extensively evaluated. The compound imparted some water and oil repellency to six fabrics made from various types of fibers; to leather; and to nylon-wood pulp and cellulose papers. In comparison with FC-208, a commercial fluorocarbon, perfluorocaprylamidomethylpyridinium chloride had good durability to laundering, but poor durability to dry cleaning. Good oil repellency was obtained on cotton fabric with as little as 2% of perfluorocaprylamidomethylpyridnium chloride.

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PART I. DEVELOPMENT OF AN EXPENDABLE MILITARY FIELD OVERGARMENT WITH PROTECTION AGAINST CHEMICAL WARFARE AGENTS IN LIQUID FORM

I. INTRODUCTION

The major initial objective of this research project for the Quartermaster Research and Engineering Command (now United States Army Natick Laboratories) was to develop an inexpensive, lightweight, expendable military field overgarment that would provide protection against chemical warfare agents in liquid form and that would be comfortable and durable enough to be worn for 6 hours under combat conditions. Additional objectives of later portions of the project are described in Parts II, III, and IV of this report.

The program for the development of an expendable overgarment involved a review and evaluation of the available information on films, foams, woven fabrics, nonwoven fabrics, and papers that might be of use for overgarments; laboratory screening evaluation of the more promising of these materials; the development of new materials and treatments to produce desired qualities; and the design and production of overgarments for field trials.

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II. SUMMARY AND DISCUSSION

The initial goals for the expendable overgarment that were established in conference with the Project Officer toward which material development was to be directed were:

Cost - not over $5.00 per garment

Weight - approximately 2 pounds or less per garment. It was estimated that about 7 square yards of material would be required for a garment, and that 50 to 80% of the final weight would be proofing agents; hence, the weight of the base material should not exceed 2.5 ounces per square yard.

Permeability - the finished garment should be sufficiently permeable to air and moisture vapor to permit wearing the overgarment for at least 6 hours without excessive discomfort.

Fire protection - the finished garment material should not increase the hazards of fire and thermal exposure.

Serviceability - the garments should remain serviceable and provide protection against chemical warfare agents in liquid form for at least 6 hours under combat conditions.

Consideration of other requirements was postponed until these basic requirements had been satisfied.

The overgarment was envisaged initially as a complete covering for the body from the neck down, with the hand and foot coverings as either integral or accessory parts. Head protection would be provided by the plastic hood that is used with the gas mask. The major part of the program on overgarment materials was concerned with development of materials for the body, arm, and leg covering. Special hand and foot covering materials and closures are discussed separately.

A. Evaluation of Commercially Available Materials

A review of the various commercially available materials—films, foams, woven fabrics, nonwoven fabrics, papers, and laminates of combinations of these—disclosed none that met all of the basic requirements listed above. Each type of material offered some advantages but was also deficient in some respect. In general, films were cheap, lightweight, and resistant to penetration by liquids. They had the undesirable properties of low tearing strength, poor snag resistance, impermeability to air, and very low permeability to water vapor. Foams were unsatisfactory for use as an unsupported base material for the overgarment because of generally poor tensile properties. Woven fabrics that had been used for outergarments had the desired permeability to air and water vapor, met the physical requirements, and had successfully undergone severe use trials, even under combat conditions. However, those with necessary durability and resistance to liquid, were too heavy and too costly for a lightweight, inexpensive outergarment. Coated fabrics that have been used for protective clothing were too impermeable to air and water vapor for the overgarment. Low tensile and tearing strengths, poor drape, poor resistance to abrasion, and high cost precluded the use of the commercially available nonwoven fabrics that were tested. Papers were the cheapest materials available that might be used to fabricate a lightweight garment. They were being used commercially for disposable clothing. However, previous field tests had shown that the commercially available papers were unsuitable for military garments, primarily because of low abrasion resistance and insufficient tearing strength. A wide range of commercial papers were screened to determine if the papers then available had any advantages over those previously tested, and it was found that reinforced papers treated to improve abrasion resistance appeared to have better properties for lightweight outergarments than the other commercial materials that were studied. Of the commercial papers tested, Kaycel RSR-8514 and Kaycel RSR-8525 had the best physical properties for lightweight clothing. These papers were 2.5-3.0 oz/yd^2 wood-pulp papers reinforced with strands of multifilament nylon and treated to improve abrasion resistance.

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Resistance to penetration by liquid CW agents was a prime requireme in the material for the overgarment, and an investigation to ascertain whethe this property could be imparted to papers was made. It was found that the resistance of papers to liquid CW agents was fairly independent of the pore size of the paper. Swelling, gelling, and absorbancy were investigated as possible mechanisms for obtaining resistance to CW agents, but they did not appear promising, and other finishing treatments were studied. A nylon-reinforced wood-pulp paper was used for the evaluations. Water repellents, latexes, and a CW-reactant finish (XXCC-3) were not effective for imparting CW-agent repellency to the paper, but fluorochemicals appeared promising, and comparisons were made of the then commercially available oil- and water-repellent fluorocarbon chemicals. FC-208 was the most effective repellent found in these trials. With only 2% of FC-208, liquid VX, HD, or GB agent did not penetrate the paper in 6 hours. The FC-208 was just as effective when used alone as when used with a pyridinium water repellent, such as Zelan AP or Norane R; but a small amount of Phobotex FTC, a durable textile water repellent, stabilized the emulsion of FC-208 and had no effect on the CW-agent resistance of treated paper. The presence of latex impregnant in the paper did not alter the effectiveness of the fluorocarbon repellent when it was applied as a separate treatment, but when the latex and repellents were applied from the same bath, the treated paper showed little resistance to CW agents.

B. Studies to Overcome Deficiencies of Commercial Reinforced, Wood-Pulp Papers

It was concluded from the above study that papers offered the most promising possibilities for construction of inexpensive, lightweight, expendable overgarments. Papers had the advantages of economy, light weight, permeability to air and water, and they could be treated to give protection against liquid CW agents. However, the commercially available papers were not satisfactory because of poor abrasion resistance, poor snag and tear resistance; poor handle, drape, and flexibility; and, in the case of reinforced papers, poor adhesion between the scrim and the surface layers. The development of papers with improvements in these properties appeared feasible and to provide the most promising route to a material that would meet the requirements for the overgarment.

Reinforced, wood-pulp papers were the best of the commercial papers evaluated and offered a promising starting point for the development of a satisfactory paper for the overgarment. Treatments with latexes, softeners, plasticizers, and flame retardants; paper weight and processing conditions; fibrid binders; different reinforcing materials; and adhesives were investigated for overcoming the deficiencies of the commercial reinforced, wood-pulp papers.

Latex impregnants increased the breaking strength and abrasion resistance of a commercial, nylon-reinforced paper—Kaycel 101-1, but, in general, decreased tearing strength. Of the latexes studied, the acrylic polymers Rhoplex B-15 and Rhoplex AC-33 gave the greatest improvements in the properties of the paper and had the best effects on the flexibility of the paper at -55°C and on the tackiness of the paper at 45°C. There was little choice between the two latexes, but Rhoplex B-15 was selected for more extended studies, and it was found that 25% of resin solids on the weight of reinforced paper was the optimum amount for improving the properties of the paper. A poly(vinyl chloride) resin, Geon 577, in combination with antimony oxide imparted flame resistance to the paper, but the treated paper had poor abrasion resistance.

A nylon fibrid was investigated as a binder in place of a latex, but it was found to be unsuitable for use.

Less beating of the pulp, lower temperatures for drying the waterleaf, lighter sheets, and softeners were found to improve the handle, drape and flexibility of wood-pulp papers; but plasticizers were not very effective. Some of the softeners studied also gave appreciable increases in the tearing strength of the paper, generally, at the expense of breaking strength. Because of their adverse effects on the strength of the papers, softeners could be recommended only at add-ons of less than 0.5%.

Scrims of different constructions and made of various synthetic yarns were compared as reinforcements for wood-pulp paper. Incorporation of 100-denier, multifilament yarns of cellulose acetate, nylon, or rayon in a wood-pulp paper increased the dry and wet breaking strength, tearing strength, abrasion resistance, and crease recovery of the paper. Nylon was generally more effective than other yarns in improving the properties of the paper; rayon was less effective than the others. Cellulose acetate gave the highest tearing strength. The properties of nylon-reinforced papers were improved as the strands per inch of yarn were increased from 4 x 4 to 6 x 6, but the properties were impaired upon further increasing the strands per inch to

8 x 8. As the size of the nylon yarns was increased from 100 to 210 denier, the tensile strengths of the paper increased slightly, but the abrasion resistance was greatly reduced.

A reinforcing scrim of 9 x 9 strands per inch of 70-denier nylon yarn was later evaluated with the hope that this scrim would give papers with improved abrasion resistance, but it was concluded that 6 x 6 strands per inch of 100-denier nylon was the better construction.

Although reinforcement of wood-pulp paper with scrim increased the strength, abrasion resistance, and crease recovery of the paper, the use of a scrim as a reinforcing material had several drawbacks: the snag resistance of scrim-reinforced paper was poor, the adhesion of the surface layers of paper to the scrims was not as great as desired, and permanent distortions could occur easily in the diagonal direction. Studies of calendered nylon textryls as reinforcing materials was undertaken in attempts to overcome these deficiencies, but the textryls were found to be unsatisfactory.

The adhesion between layers of wood-pulp paper and nylon scrim was increased by treating the scrim with adhesives. Of the adhesives tested, Ubabond H-511 (an acrylonitrile-rubber adhesive) gave papers with the highest peel strength, and 13% of adhesive solids appeared to be a desirable level of add-on to use.

In addition to the protection against liquid CW agents that was needed in a paper for the protective overgarment (which could be obtained by treatment with FC-208) it was desirable that the paper be flame resistant, at least enough so to avoid any special hazard when subjected to high-energy thermal radiation. Numerous non-durable, semi-durable, and durable flame retardants were evaluated for flame proofing a nylon-reinforced wood-pulp paper containing 20% of an acrylic binder. Three flame retardants were found that were effective—Fi Retard NBX; a mixture of ammonium sulfamate, diammonium phosphate, and carboxymethylcellulose in the proportions of 7.2 : 2.8 : 1, respectively; and Apex Flameproof 290-B. However, only Apex Flameproof 290-B was an effective flame retardant in the presence of FC-208 without decreasing CW agent repellency.

As a result of these studies, a lightweight (4-oz/yd^2) wood-pulp paper reinforced with 6 x 6 strands per inch of 100-denier nylon containing 11% Ubabond H-511 scrim adhesive, 20% Rhoplex B-15, and 2-4% FC-208 (percentages on final weight) was the best experimental material prepared for the overgarment. This experimental paper had excellent resistance to liquid CW agents, good flame retardancy, and physical properties superior in many respects to the best of the commercial materials. However, it had very poor handle, drape, and flexibility and extremely low air permeability. Some improvements in handle, drape, and flexibility could have been obtained with softeners or mechanical treatments in exchange for lower levels of physical properties, but the low air permeability would still have remained a serious disadvantage. The use of cotton linters in place of wood pulp did not overcome these deficiencies.

C. Experimental Synthetic-Fiber Papers

Since the physical properties of the wood-pulp papers were not satisfactory for the overgarment, studies were undertaken to determine whether the desired properties could be obtained with reinforced, synthetic-fiber papers.

For selection of the most appropriate fibers for use in the papers, nonreinforced papers were prepared from the following seven fibers alone and in various combinations: rayon, RD-101 (a multi-cell rayon fiber), nylon, poly(vinyl alcohol), cellulose acetate, ordinary Dacron, and Dacron D-90 (a polyester fiber that crimps on heating). Wood-pulp fiber was used in many of the papers because of its desirable general properties, its good paper-making qualities, and its low cost. From an evaluation of the properties of the papers, nylon was found to be the most desirable of the synthetic fibers; and papers containing 50% nylon and 50% wood pulp had the best balance of physical properties. The tearing strength and abrasion resistance of a 50:50 nylon-wood pulp paper treated with Rhoplex B-15 were greater than for the commercial synthetic-fiber papers evaluated; breaking strength was about the same; and the abrasion resistance was slightly greater than the abrasion resistance of Kaycel RSR-8525, one of the best of the commercial papers. However, Kaycel RSR-8525 had higher dry and wet breaking strengths and tearing strengths which were probably due to the reinforcing scrim that it contained. The nylon-wood pulp paper had much higher air permeability and better handle and flexibility than the all wood-pulp paper.

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An experimental nonreinforced paper containing 75% Dacron D-90 and 25% wood pulp had excellent handle, drape, and flexibility; but the abrasion resistance and breaking strength of the paper were too low for protective overgarments.

The following materials were evaluated as reinforcing agents for the 50:50 nylon-wood pulp paper: scrims made from cotton, rayon, polyethylene, poly(vinylidene chloride), and nylon yarns; nonwoven fabrics made from all nylon, all cellulose acetate, all viscose, and a 50:50 mixture of cellulose acetate and viscose fibers; nylon textryl papers; and a lightweight nylon fabric. The nylon scrim was the most effective of the various materials tried, and 6 x 6 strands per inch of 100-denier nylon yarn was the best construction for the scrim. Splic-It was the best of a number of adhesives evaluated for bonding the scrim to the paper.

A 3.0 oz/yd^2 paper containing 50% nylon and 50% wood pulp reinforced with a 6 x 6 scrim of 100-denier nylon and treated with an acrylic binder had excellent physical properties and appeared to be a satisfactory base material for construction of the expendable protective overgarment. Good resistance to liquid GB, HD, and VX agents was obtained by treating the material with FC-208; and no loss in protection of the treated material occurred after soiling, abrading, wetting, or creasing. The treatment imparted water repellency to the reinforced nylon-wood pulp paper, but the treated paper was not rain resistant. Attempts to obtain both liquid CW agent resistance and rain resistance with mixtures of FC-208 and a pyridinium type water repellent (Norane R) were not successful. However, rain resistance was only a desired and not an essential property of the material for the overgarment.

Numerous flame retardant treatments were investigated for use on reinforced nylon-wood pulp paper bonded with Rhoplex B-15 and treated with FC-208 to make it resistant to CW agents, but no satisfactory method was found for making the candidate paper for the overgarment flame resistant. The most satisfactory of the various flame retardants that were investigated was a treatment with tetrakis(hydroxymethyl)phosphonium chloride and tris(1-aziridinyl)phosphine sulfide in a ratio of 1:1. However, the lack of commercial availability and the poor stability of APS made the use of this treatment impractical.

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A nylon-wood pulp paper containing poly(vinyl chloride), antimony trioxide, and FC-208 was resistant to flame and to liquid CW agents. However, the paper was not as satisfactory in regard to hand, drape, flexibility, and abrasion resistance as the reinforced nylon wood-pulp paper containing the acrylic binder.

D. Experimental Paper 2-2-62

A 3.0 oz/yd^2 nylon-wood pulp paper was accepted by the Project Officer as a candidate material for the preparation of the protective over-garment. The material consisted of two 50%-nylon and 50%-wood pulp sheets reinforced with an adhesive-bonded 6 x 6 scrim of 100-denier nylon yarn, treated with an acrylic polymer (Rhoplex B-15) to bond it and increase abrasion resistance, and treated with a fluorochemical (FC-208) to provide water repellency and resistance to liquid CW agents. Compared to the two best commercial papers found, the nylon-wood pulp paper had the highest breaking strength, bursting strength, puncture strength, and abrasion resistance. The commercial papers had better handle and drape and higher tearing strength.

About 1700 yards of a reinforced, nylon-wood pulp paper, as similar as was practical in the construction to the laboratory-prepared paper described above, was made on plant equipment by the Kimberly-Stevens Corporation for laboratory and field evaluations. Prior to the production of this yardage, a trial production run was made to establish the feasibility of making the paper on the commercial equipment and to determine suitable processing conditions for production. The finished paper, identified as Experimental Paper 2-2-62, weighed 3.2 oz/yd^2, had excellent physical properties, and, for a paper, had good drape and handle. Experimental Paper 2-2-62 was made from two sheets of paper that contained 30% of 3.0 denier, 0.37-inch nylon; 20% of 1.5 denier, 0.25-inch nylon; and 50% of Harmac kraft laminated with an adhesive [poly(vinyl chloride)-plastisol-Adhesive KS-1] to a nonwoven scrim containing 6 x 5 strands per inch of 100-denier nylon yarn. The laminate was treated with Rhoplex B-15 (an acrylic polymer) to apply 25% solids, and then the Rhoplex-treated paper was treated with FC-208 to apply 3% solids.

From field studies by the U. S. Army Natick Laboratories, the paper was estimated to have a useful life of about 3 to 4 hours under combat conditions. The major deficiencies of the paper were poor abrasion resistance when wet, poor snag resistance, and delamination. The tearing breaking, and bursting strengths, as well as the hand, drape, and flexibility of the paper appeared to be satisfactory. Dry abrasion resistance was satisfactory when double layers of paper were used at the elbows and knees of the garments.

Based on laboratory data, somewhat better performance would have been expected if Experimental Paper No. 8-28-61 had been used. This paper probably would not have delaminated in use, and its abrasion resistance and puncture strength were better. This paper is similar to the plant-prepared Experimental Paper No. 2-2-62 except that the base sheet is made from 50% of 1.5-denier, 0.35-inch nylon and 50% wood pulp. This composition was recommended for the plant production, but there was not enough time to obtain a sufficient amount of 1.5-denier nylon and have the paper ready in time for the field studies.

The resistance to liquid CW agents of Experimental Paper No. 2-2-62 was satisfactory. Even samples of the paper taken from worn areas of the field-worn garments were resistant to penetration by the agents.

E. Studies to Overcome Deficiencies of Experimental Paper 2-2-62

The physical properties of the candidate paper most needed to be improved, as shown by the results of the field trials, were wet abrasion resistance, puncture (or snag) resistance, and adhesion of the base sheets to the scrim. Binders, increased paper weights and densities, scrim adhesives, and other reinforcing materials were investigated for improving these properties.

Several latex binders and fibrids were investigated for improving the wet abrasion resistance of the candidate paper, and the use of Rhoplex HA-12 as binder more than doubled the wet-abrasion resistance of the paper.

Increasing the unit weight of the base sheet increased the abrasion resistance, puncture strength, and bursting strength, and slightly decreased the air permeability of the paper. Even slight increases in the weight of the base sheet were beneficial. Therefore, it was concluded that it would be desirable to increase the weight of the base sheet used in the reinforced paper even though minimum weight was desired.

Preliminary data showed that an increase in the density of the base paper increased the puncture resistance, but also greatly decreased the air permeability of the paper.

Improved scrim adhesives were found that appeared to be suitable for use on plant equipment, but Kimberly-Stevens could not use them because of mechanical instability, plugging of lines in the equipment, or undesirable tack time. Consequently, optimum conditions of application were established for producing high-peel-strength papers with an adhesive similar to the one used in the previous plant trials (Adhesive KS-2).

A method was developed for dyeing the paper to an OD shade without detracting from other properties, and dry creping was found to improve the hand and flexibility.

F. Experimental Papers 6-21-62 R and 6-21-62 GCD

On the basis of the above results, two scrim-reinforced nylon-wood pulp papers with improved physical properties over Experimental Paper 2-2-62 were developed, and they were produced on commercial equipment at Kimberly-Stevens. The papers consisted of two 50% nylon (1.5 denier, 0.25-inch) and 50% wood-pulp (Harmac kraft) sheets reinforced with a 6 x 5 scrim of 100-denier nylon yarn treated with Adhesive KS-2. One paper, identified as Experimental Paper 6-21-62 R, was treated with Rhoplex HA-12, dye, and FC-208; the other paper, identified as Experimental Paper 6-21-62-GCD, was treated with Geon 577, antimony trioxide, dye, and FC-208. Experimental Paper 6-21-62 GCD was dry creped to improve hand and flexibility, but because of processing problems encountered, Experimental Paper 6-21-62 R was not creped.

The improved papers both weighed 3.9-4.7 oz/yd^2 and were estimated to cost less than $0.75 per square yard. They had high air permeability; very good physical properties, including wet-abrasion resistance, snag resistance, and adhesion of the base sheet to the scrim; and satisfactory resistance to liquid CW agents. However, the papers had poor hand, drape, and flexibility. The results of field evaluations of the papers indicated that they had a service life under combat conditions of 3-4 days. (The evaluations were carried out on the Cotton Fabric Course at Fort Lee, Virginia, by the U. S. Army Research and Engineering Field Agency.) Hence, except for weight, the papers had the military characteristics desired of the expendable, CW-agent-protective field overgarment.

G. Experimental Nonwoven Fabrics

Experimental nonwoven fabrics made from nylon, rayon, and nylon-rayon blends and treated with different binders were evaluated in an effort to find base materials for the overgarment superior to the experimental papers. The results of the evaluations indicated that an overgarment made from a nonwoven fabric would probably have the advantages of improved durability, flexibility, hand, and drape; and the disadvantages of higher cost and weight and of lower (though possibly satisfactory) resistance to liquid CW agents.

The optimum composition of a nonwoven fabric for the overgarment was not established. However, of the fibers and fiber mixtures evaluated, nylon was the best; and, of the binders evaluated, a 1:1 solids mixture of Rhoplex HA-12 and Rhoplex HA-8 was the best. Laminates of the experimental nonwoven fabrics to a lightweight nylon parachute fabric were not encouraging for use in the overgarment.

H. Overgarment Design Studies

Work on the design of the overgarment was begun at Southern Research Institute but was completed at International Latex Corporation, Dover, Delaware, under subcontract D-7933. Many overgarments of different designs were made and studied; and, of these, a one-piece coverall-type overgarment and a two-piece pajama-type overgarment designed by International Latex Corporation was approved by the Project Officer. Field evaluations of the two overgarments fabricated from Experimental Papers 6-21-62 GCD and 6-21-62 R by the U. S. Army Natick Laboratories indicated that the one-piece design was more desirable.

Adhesives were investigated for forming seams and several were found that were satisfactory. However, sewn seams painted with an adhesive were also satisfactory and were considered more desirable, since they were more amenable to current garment manufacturing conditions.

We gave some attention to the fabrication of protective gloves and boots, but the study was taken over by the U. S. Army Natick Laboratories before being completed in order to allow us to devote more effort to other studies. At the termination of our research work on gloves and boots, we had found that nylon film appeared to be a good candidate material for construction of these items. However, work at Natick revealed that poly(vinyl chloride) and polyethylene films were also acceptable candidate materials; and, at the Project Officer's request, 25 sets of gloves and 25 sets of boots were made from each of the materials by International Latex Corporation, under subcontract with us, and sent to the Natick Laboratories for evaluation.

III. BASE MATERIAL FOR OVERGARMENT

A. Evaluation of Commercially Available Materials

At the start of this project a survey was made of the commercially available materials to determine which, if any, of these might be of use in preparing a protective garment that would meet the established requirements for an inexpensive, lightweight overgarment that would provide protection against liquid chemical-warfare agents. Films, foams, woven fabrics, nonwoven fabrics, and papers were considered. N commercially available material was found that had all of the qualities required for the overgarment. In evaluating the usefulness of a material for this application, primary consideration was given to the following criteria: it should (1) provide protection against liquid CW agents, (2) be durable enough to be worn under combat conditions for a minimum of 6 hours, (3) not impose undue heat stress on wearer, (4) be lightweight (about 4 oz/yd^2 maximum), (5) not be a thermal hazard, and (6) be low in cost.

1. Films and foams

A summary of published data on the properties of commercially available plastic films is given in Table I-1. These data are for standard films of various polymers. Data on some special types of films and sheet foams are given in Table I-2.

Films have many features that are desirable for the protective overgarment, such as lightweight, good flexibility (except at very low temperatures), good tensile strength, and low cost. Major disadvantages are generally low tearing strength, poor snag resistance, low air permeability, and low water-vapor transmission.

Table I-1. General Range of Physical Properties of Conventional Commercial Plastics Films[a]

Type of Plastic	Polyamide	Poly(trifluorochloroethylene)	Polyethylene		Polypropylene	Poly(ethylene terephthalate)	Vinyl chloride-acetate copolymer (nonrigid)	Vinylidene chloride-Vinyl chloride copolymer	Polytetrafluoroethylene
			Low density	High density					
Tensile strength, psi	9,000-12,800	6,300-6,600	1,350-2,500	2,400-6,100	5,000-10,000	17,000-23,700	2,000-4,500	8,000-20,000	1,500-4,000
Elongation at break, %	50-240	90-300	200-800	10-650	over 200	35-110	150-500	20-140	100-350
Tearing strength, g[b]	1300	200-350	60-200	15-300	32-1,750	10-27	30-14,00	10->100	10-100
Folding endurance	-	-	very high	very high	very high	20,000	-	>500,000	-
Water vapor permeability (g/24 hr/m^2/mm thickness/cm Hg at 25°C)	0.3-1.8	0.00	0.04-0.06	0.02-0.04	0.06	0.05-0.15	0.23	0.01-0.03	0.0
Permeability to gases (10^{-4} g/24 hr/m^2/mm thickness/cm Hg at 21°C, 0% RH)	CO_2 165 O_2 26 (50% RH)	-	CO_2 12,000 O_2 19,000 N_2 400	CO_2 6,200-3,300- O_2 800-950 N_2 100-50		CO_2 <0.5 O_2 <0.5 N_2 <0.5	-	CO_2 12 O_2 2.4 (50% RH)	-
Water absorption, 24 hr, %	1.0-1.5	0.00	0.08	nil	0.005 or less	<0.5	negligible	negligible	0.00
Bursting strength, 1 mil thickness, Mullen, lb	-	42 (2 mil)	-	-	-	45-60	20	25-35	-
Resistance to heat, °C	82-192	149	93	121	38-104	149	65-104	65-104	260

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[a] Data from Modern Plastics 37, 532 (1960), except (c).

[b] Elmendorf tear

[c] Data from manufacturer of film listed.

Table I-1. (continued)

Type of Plastic	Rubber hydrochloride	Vinyl-nitrile rubber	Poly(vinyl fluoride)[c]	Methyl cellulose[c]	Polystyrene (oriented)	Poly(vinyl alcohol)[c]	Poly(vinyl chloride) (nonrigid)	Cellulose acetate
Tensile strength, psi	3,500-5,000	2,500-4,000	7,500	4,200-4,700	7,100-12,100	4,000-10,000	150-500	5,400-13,900
Elongation at break, %	200-800	250-500	230	40	3-10	180-600	20	25-45
Tearing strength, g[b]	60-1,600	200-960	80			250-800	60-1,400	2-25
Folding endurance	250,000	very high						250-400
Water vapor permeability ($g/24\ hr/m^2/mm$ thickness/cm Hg at 25°C)	0.007-0.23	-	1	80	0.5-0.7	4	0.35-2.0	1.4-8.8
Permeability to gases ($10^{-4}\ g/24\ hr/m^2/mm$ thickness/cm Hg at 21°C, 0% RH)	CO_2 288-13,500 O_2 38-3,250	low	CO_2 1.4 O_2 0.3 N_2 0.02	CO_2 400 O_2 80 N_2 29	CO_2 1080 O_2 2420 N_2 49.5 Air 105	CO_2 200 O_2 120	CO_2 970 O_2 150 (50% RH)	CO_2 12,000-17,500 O_2 1,700-2,500 N_2 160
Water absorption, 24 hr, %	5	negligible		soluble	0.04-0.06	30	negligible	3.6-6.8
Bursting strength, 1 mil thickness, Mullen, lb						250-800	20	30-70
Resistance to heat, °C	87-96	93		243	79-93	good	65-104	65-104

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[a] Data from Modern Plastics 27, 532 (1960), except (c).

[b] Elmendorf tear.

[c] Data from manufacturer of film listed.

Low water-vapor transmission is probably the most insurmountable drawback to the use of standard films in the overgarment. It has been found[1] that the approximate loss of body weight by perspiration is 0.2 lb/hr (90 g/hr) for a man at rest with an ambient temperature of 21°C (70°F); for a man doing 90,000 ft-lb of work per hour with an ambient temperature of 16°C (60°F) the loss in body weight by perspiration is 0.5 lb/hr (225 g/hr). Assuming that an overgarment would contain about 7 m^2 of film, the film would be required to transmit water vapor at a rate of about 30 $g/hr/m^2$ or 720 $g/24\ hr/m^2$ to maintain the comfort of the wearer of the garment. Some investigators[2] have reported even this rate of water-vapor transmission, alone, is not sufficient for comfort.

Assuming that a thickness of at least 3 mils would be required for adequate strength in a film, the rate of water-vapor transmission of an acceptable film would have to be over 2000 $g/24\ hr/m^2/mil$ or over 50 $g/24\ hr/m^2/mm$. Only one of the types of films listed in Table I-1, methyl cellulose with a water-vapor permeability of 80 $g/24\ hr/m^2/mm$, meets this requirement, and methyl cellulose cannot be used because it is water soluble. Of the hydrophobic commercial films, cellulose acetate has the highest reported water-vapor permeability, a maximum of 8.8 $g/24\ hr/m^2/mm$, but this value is less than one-half of that required to pass the amount of perspiration from an inactive man at only a moderate ambient temperature.

Other properties of these films that would make them unsatisfactory for use in overgarments are their low tearing strengths and the ease with which they can be snagged or punctured. Polypropylene has the highest tearing strength, up to 1700 g (3.7 lb), of the films listed in Table I-1; but this value is low compared to the tearing strengths of woven fabrics. The resistance to heat of most of the plastic films is poor; most of those listed will not withstand temperatures above 93°C (200°F).

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[1] Heating, Ventilating, and Air Conditioning Guide, p. 64, American Society of Heating and Air Conditioning Engineers, Inc., New York 1959.

[2] F. N. Craig, H. W. Garren, H. Frankel, and H. W. Blevins, J. Applied Physiology 6, 634-644 (1954).

In addition to these conventional films, three special types of commercially available films and one sheet foam were investigated for utility in the overgarment. These materials were: poly(vinyl alcohol) film that was reported to be permeable to water vapor, but not to air; a poly(vinyl chloride) film that is used in a disposable safety suit; a microporous film; and a thin sheet of polyurethane foam. The physical properties of these materials were determined with results as given in Table I-2.

All three of these films had very good resistance to abrasion. The microporous film, Herculite's Micro-Vent, contained a reinforcing scrim, and it had exceptional tensile properties (breaking strength, 72-76 lb/in. and tearing strength, >3200 g). The low air permeabilities of these films would make them unsuitable for the overgarment.

The tensile properties of the Scottfoam were very poor; the breaking strength was low, only 2.5 to 3.1 lb/in., and the tearing strength was only 314 to 326 g. The abrasion resistance of the foam was good and its air permeability was very high, but the foam was not considered satisfactory for use as an unsupported base material for the overgarment because of its poor tensile properties.

Based on these data, none of the commercially available plastic films appeared to offer promise for use in preparing the protective overgarment.

2. Woven fabrics

Woven fabrics are, of course, widely used in garments of all types and are available in a wide range of weights and weaves. They were, therefore, a prime consideration in the search for a suitable material for the protective overgarment. The major questions regarding the use of woven fabrics were concerned with the special requirements of light weight with adequate serviceability, low cost, and liquid resistance.

Table I-2. Properties of Special Commercial Films and Foams

Films and foams	Manufacturer	Description	Weight, oz/yd²	Thickness, mils	Breaking strength,[a] lb/in.				Elongation at break, %				Elmendorf tear, g				Abrasion resistance		Air permeability, ft³/min/ft², 0.5 in. water
					Dry		Wet		Dry		Wet		Machine		Cross				
					Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Range	Average	Range	Average	Cycles	Weight loss, %	
Reynolon 4-6	Reynolds Metals Co.	Poly(vinyl alcohol) film	4.0	5.0	38.4	47.0	21.2	17.8	447	504	954	900	1760-2464	1978	1600-2016	1801	200	0.64	<0.5
Disposable Safety Suit	Safety First Supply Co.	Poly(vinyl chloride) film	3.0	5.5	11.6	4.6	11.0	4.6	201	181	231	146	192-198	194	240-672	502	200	1.25	<0.5
Herculite Micro-Vent	Herculite Protective Fabrics, Inc.	A microporous film containing a scrim	4.0	9.5	76.2	72.2	69.8	57.6	65	69	57	39	>3200		>3200		200	0.60	<0.5
Scottfoam	Scott Paper Co.	Polyurethane foam	1.5	12.5	3.1	2.5	2.7	2.7	369	388	472	396	288-336	314	288-320	326	162	0.32	>455

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[a] Breaking strength determined on 0.5 in. strips and converted to lb/in.

A review of the literature provided no useful information on the serviceability of lightweight woven fabrics (not over 4 oz/yd^2) under conditions approximating those to which the protective overgarment would be subjected. The physical properties of several selected types of commercially available lightweight woven fabrics were determined and compared with those of other types of materials, and the feasibility of treating standard woven fabrics to make them repellent to liquid CW agents was investigated. Commercially available coated fabrics were also included in these evaluations.

a. Uncoated woven fabrics

The uncoated woven fabrics normally used for military clothing have many physical properties desired in the protective overgarment, and certain impregnants can provide the required resistance to CW agents. However, because of weight and price, the presently used fabrics were unsatisfactory for the expendable overgarments and a brief investigation was made of the properties of commercially available lightweight woven fabrics.

(1) Physical properties of selected lightweight woven fabrics

The commercial fabrics were selected for initial evaluation of physical properties. These were: a 2.5 oz/yd^2 nylon fabric, a 2.5 oz/yd^2 Dacron fabric, and a 4 oz/yd^2 cotton sheeting. Descriptions of the fabrics and data on their properties are given in Table I-3. In comparison with the commercial films, foams, and papers that were evaluated, the lightweight fabrics were superior in drape, hand, tearing, and breaking strengths and abrasion resistance. The nylon and Dacron fabrics both had higher breaking strengths and air permeabilities than the cotton fabric. The Dacron fabric had poor apparent abrasion resistance, but this was a result of the loose weave of the fabric, which caused the fabric to come apart rather than to abrade. The nylon fabric had better abrasion resistance on an actual weight loss basis than the cotton fabric; 0.61% weight loss, or 0.027 oz/yd^2 for cotton. The tearing strengths of the nylon and Dacron fabrics could not be determined because the yarns pulled out of the fabrics during the tests.

Table I-3. Properties of Commercial Woven Fabrics

					Breaking strength,[a] lb/in.				Elmendorf tear, g				Abrasion resistance		
					Dry		Wet		Machine		Cross				
Woven fabrics	Manufacturer	Description	Weight, oz/yd²	Thickness, mils	Machine	Cross	Machine	Cross	Range	Average	Range	Average	Cycles	Weight loss, %	Air permeability, ft³/min/ft², 0.5 in. water
Nylon Style 1181	Burlington Fabric Industries, Inc.	210 denier warp and filling, scoured and heat set	2.5	5.7	109	106	99	114	b	b	b	b	200	0.61	88
Dacron Style 1295	Burlington Fabric Industries, Inc.	Scoured and heat set	2.5	6.6	81	41	78	92	b	b	b	b	40	3.44	>455
Cotton O.D.	Obtained from U.S. Army Natick Laboratories	48 x 48 cotton sheeting	4.0	13.1	49	44	62	56	1504-1696	1626	1600-1920	1690	200	0.67	117

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[a] Determined on J-2 Model Scott Tester.

[b] Yarns pulled out without tearing fabric.

Of these three fabrics, the 4-oz cotton sheeting would be the best choice for the overgarment.

(2) Feasibility of making lightweight woven fabrics resistant to CW agents

Two types of treatments were investigated for effectiveness in making 10 types of woven fabrics resistant to penetration by liquid CW agents. The fabrics are described in Table I-4.

(a) FC-208—Phobotex FTC treatment

The 10 woven fabrics described in Table I-4 were treated by padding to apply 2%, 4%, and 8% of FC-208 fluorochemical solids combined with 0.25% of Phobotex FTC solids and then dried 5 minutes at 150°F. The resistance of the fabrics treated to apply 2% of FC-208 solids was determined with all three agents (HD, GA, and VX) by the standard drop test and with VX agent by the expulsion test; only resistance to VX agent was determined (drop and expulsion tests) for the fabrics treated with 4% and 8% of FC-208.

The crepe, percale, cotton chiffon, polypropylene fabric, and textured nylon fabrics treated to apply 2% FC-208 were not penetrated by any of the agents in the drop test, but all of these fabrics except the polypropylene fabric were penetrated by VX agent in the expulsion test. With 4% or 8% applications of FC-208, the batiste and the linen were not penetrated by VX agent, but the nylon chiffon, the organdy, and the pique were penetrated in the drop test; however, the batiste and linen were penetrated in the expulsion test.

Although the polypropylene fabric was not penetrated by any of the agents in these tests, the fabric had very low permeability after the treatments and was stiff and leathery. None of the ten fabrics treated with FC-208 and Phobotex FTC was considered acceptable for use in the overgarment.

Table I-4. Description of Fabrics Treated and Evaluated for CW Resistance

Type of material	Fiber content	Source	Weight, oz/yd²	Cost, per yard	Construction Ends/in.	Construction Picks/in.
Percale	100% cotton	Sears Roebuck and Company	3.4	0.33	71	57
Batiste	100% combed cotton	Sears Roebuck and Company	2.2	0.46	86	69
Crepe	73% arnel triacetate 27% nylon	Sears Roebuck and Company	2.9	0.93	165	92
Linen	100% Irish linen (imported)	Sears Roebuck and Company	3.3	1.17	69	97
Pique	100% Dacron polyester	Sears Roebuck and Company	2.5	1.37	107	83
Nylon chiffon	100% nylon	Sears Roebuck and Company	1.1	0.74	110	92
Organdy	100% Egyptian combed cotton	Sears Roebuck and Company	1.5	0.93	87	66
Cotton chiffon	100% pima cotton	Sears Roebuck and Company	3.4	1.27	125	78
Textured nylon	70 denier textured nylon in warp 140 denier nylon yarn in filling	Georgia Institute of Technology	5.0	-	190	105
Polypropylene	100% polypropylene	Burlington Industries, Inc.	4.8	-	56	43

Mr. L. J. Weiner of the United States Army Natick Laboratories suggested a 2 oz/yd^2 acetate fabric as a low cost fabric that might be utilized in making the protective overgarment. The fabric was calendered under heat and pressure to reduce the air permeability from approximately 105 to 18 ft^3/min/ft^2. As shown in Table I-5, neither this "closed" fabric nor the control fabric was resistant to liquid VX agent, before or after applying 3% FC-208 or after applying 3% FC-208 solids and 25% Rhoplex B-15 solids.

(b) Quarpel treatment

The Quartermaster Research and Engineering Command supplied the following Quarpel-treated fabrics for evaluation of resistance to liquid CW agents: a 9.0 oz/yd^2 cotton sateen, a 6.5 oz/yd^2 cotton oxford, and a 3.6 oz/yd^2 cotton printcloth. These fabrics were compared with a 4.0 oz/yd^2 cotton printcloth treated by padding to apply 2% FC-208 and 0.25% of Phobotex FTC solids. The resistances of the treated fabrics to liquid HD, GA, and VX agents were determined by the standard drop test and expulsion test. The treated fabrics were also evaluated for resistance to liquid VX agent after creasing and after soiling. The data obtained are given in Table I-6. The only fabric that was resistant to all agents under the various test conditions was the 9.0 oz/yd^2 cotton sateen treated with Quarpel. All of the other treated materials failed one or more of the tests. The 9.0 oz/yd^2 cotton sateen would not be acceptable for the overgarment because of its high weight.

b. Coated woven fabrics

Coated woven fabrics were expected to have about the same disadvantages as films in low permeability to air and water vapor. However, two coated fabrics that were claimed to have some permeability to water vapor were evaluated.

Table I-5. Resistance of Acetate Taffeta[a] to VX Agent

Treatment	Air permeability, $ft^3/min/ft^2$, 0.5 in. water	Drop test[b]		Expulsion test[c]	
		Samples evaluated	Samples penetrated	Samples evaluated	Samples penetrated
A. Not calendered					
3% FC-208	153	2	2	5	5
25% Rhoplex B-15 3% FC-208	22	2	1	5	4
B. Calendered					
3% FC-208	130	2	1	5	5
25% Rhoplex B-15 3% FC-208	19	2	0	5	5

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[a] 2.0 oz/yd^2 before calendering or treatment.

[b] Six drops per sample.

[c] One drop per sample.

Table I-6. Resistance of Quarpel-Treated Fabrics to CW Agents

Fabric	Treatment	Air permeability, $ft^3/min/ft^2$, 0.5 in. water	Standard drop test			Expulsion test			Standard drop test with VX for	
			HD	GA	VX	HD	GA	VX	Soiled specimen	Creased specimen
Cotton sateen	Quarpel	3	a	a	a	a	a	a	a	a
Cotton oxford	Quarpel	3	a	b	c	c	c	c	c	c
Cotton print	Quarpel	28	a	a	c	c	c	c	c	a
Cotton print	FC-208	2	a	a	a	c	a	c	c	a

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[a] No penetration during test period. Duration of standard drop test is 6 hours. Duration of expulsion test is 1 minute.

[b] Some drops penetrated, others did not penetrate during 6 hour test period.

[c] Penetrated instantly.

One of these was a fabric having a microporous coating that was reported to be water repellent and water-vapor transmitting. This fabric, made by Reeves Brothers, Inc. and designated Durado poplin, had a coating containing pores reported to have diameters of 3 to 12 microns.[3] The breaking strength of the coated fabric was approximately equivalent to that of the 4.0 oz/yd^2 cotton sheeting, but its tearing strength and abrasion resistance were less than those of the sheeting. The air permeability of the coated fabric was less than 0.5 ft^3/min/ft^2 which made it unsuitable for the overgarment.

The second coated fabric examined was a neoprene-coated light-weight nylon fabric from Tennessee Eastman Corporation that was reported to be nonporous to air, but to have a high water-vapor transmission rate. The fabric construction was 117 x 76, 2 x 1 twill, 40-denier nylon warp and 70-denier nylon filling. The water-vapor transmission rate of the fabric was 3.0-3.3 g/hr/m^2 with 100% RH on one side and 40-50% RH on the other side, and the air permeability was 0.5 ft^3/min/ft^2 at a pressure of 0.5 in. water. This rate of water vapor transmission is well below the minimum requirement of 30 g/hr/m^2 as discussed previously.

Most of these studies of commercially available woven fabrics were made early in the program and the results indicated that the available fabrics were less promising than papers for meeting the requirements established at that time for the expendable, low-cost, light-weight overgarment with resistance to liquid CW agents.

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[3] Textile World 110, 73 (1960).

3. Papers

a. Background information

Papers have been extensively studied for use in disposable clothing in recent years. The properties and performance of four papers that had been field tested for use as military garments were supplied to us by the U. S. Army Natick Laboratories.[4] These papers were Kaycel 101-1, Masslinn RI-1150, Johnson and Johnson's M840B, and material composed of two layers of cellulose wadding with an interlayer of nonwoven nylon scrim. The scrim in the last fabric was composed of 6 x 5 strands per inch of 100-denier multi-filament nylon yarn; the cellulose wadding was treated to make it fire and water resistant. The Kaycel 101-1 was a similar material, but the cellulose wadding was described as a bleached sulfite pulp. Masslinn RI-1150 was described as a mixture of cellulose acetate and rayon bonded with a latex, and Johnson and Johnson's M840B as a rayon bonded with a resin in a diamond pattern. The data supplied in the physical properties of these papers are in Table I-7. From the results of field tests of these papers, it was concluded that none of these papers was suitable for military garments. The principal deficiencies were low abrasive resistance and low tear strength, especially when wet. The investigators found that the abrasion resistance of the papers could be improved by impregnating those with various polymers, the best of which was neoprene. In tests of abrasion resistance by dragging the material weighted with a 10-lb sack of sand in a gritty road, unimpregnated papers could be dragged only about 25 yards before rupture, whereas neoprene-impregnated papers could be dragged 8 to 10 times as far before rupture.

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4. Snell, Elliot, "Evaluation of Commercial Disposable Clothing," Report 2, Quartermaster Research and Engineering Command (Project Reference 7-9-3-30-001), November, 1958.

Table 1-7. Physical Properties of Papers Field-Tested in Garments

Property	Johnson and Johnson's M840B	Kaycel Type 101-1	Masslinn BI-1150	See ref. Snell
Weight, oz/yd^2	1.76-1.96	3.3	2.45	3.6
Thickness, mils	11	9	13	11.7
Tensile strength, lb/in.				
Dry, machine direction	25.3	6.8-11.2	9.9-11.0	14.7
Wet, machine direction		7.4	5.0	7.5
Dry, transverse direction	3.6	8.1	5.1-5.7	13.3
Wet, transverse direction		5.4	3.0	6.5
Elongation, %				
Machine direction	15	16	13	
Transverse direction	35		30	
Elmendorf tear, g				
Dry, machine direction	250-368	1728	464-520	66.56
Dry, transverse direction	232	1827	456-591	
Bursting strength, psi	35	25	54	35
Fold endurance, cycles				
Machine direction	4000	4000	4000	
Transverse direction	9		1630	
Tabor stiffness				
Machine direction	1.93	0.24	2.90	
Transverse direction	0.7	0.33	1.00	
Air permeability, ft^3/min/ft^2, 0.5-in. head of water	241	13.9	297	14.8
Flammability	burns	passed	failed	failed
Abrasion, cycles				56

In the development of a laminate of aluminum foil and paper for use in disposable fire-fighting clothing, Arthur D. Little, Inc., evaluated bleached and unbleached kraft paper, a rope-fiber paper, and several reinforced papers.[5] Of the papers evaluated, a 90-pound unbleached kraft paper reinforced with rayon scrim was found to be the most desirable paper for this application but because of its limited availability, a 50-pound unbleached kraft paper was used. For reinforcement, a $\frac{1}{4}$-in. mesh rayon scrim was laminated between the aluminum foil and the paper. The kraft papers had to be creped 15 to 20% to provide the minimum flexibility and drape required for clothing. The wet strength of the kraft papers, although higher than that of the other papers evaluated, was lower than desired. Soluble wet-strength kraft papers were not commercially available.

Nylon-reinforced papers that were evaluated by A. D. Little, Inc., were similar to the ones discussed earlier. Excellent drape and flexibility without creping were the desirable properties reported for the papers, and low strength and abrasion resistance were the undesirable properties. A paper reinforced with glass scrim was evaluated but was found to be unsatisfactory, because it was very stiff and had very poor flex endurance. Arledter[6] reported similar properties for papers containing reinforcing strands of glass filaments. He prepared papers from a mixture of 75% cellulose fibers and 25% 3-micron glass fibers that had better flexibility than the glass-reinforced papers, but the flex endurance of the papers was still quite low, and we do not believe they would be suitable for use in clothing.

The third type of paper that was investigated by Arthur D. Little, Inc., was the rope-fiber paper. It has an unusual fabric-like hand when dry creped, but its strength and abrasion resistance were lower than those of the unbleached kraft.

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5. Arthur D. Little, Inc., "Development of Heat-Reflective Paper-Based Laminate for Disposable Fire-Fighter's Suit," Quartermaster Research and Engineering Command, Contract No. DA-19-129-QM-1243, April 30 1959.

6. H. S. Arledter, TAPPI 39, 299-303 (1956).

Synthetic Fiber Papers. Papers have been prepared from nylon, Dacron, Orlon, Dynel, polyethylene, Acrilan, rayon, glass, steel, and aluminum. In synthetic fiber systems, in general, the fibers must be held together by some external binder system to overcome the processing problem in papermaking of insufficient strength of the wet web. To develop papers with maximum tensile properties, the fibers are bonded. Fiber bonding has been accomplished in some instances by softening portions of the fibers themselves with solvents, heat, or both, but most generally it is accomplished by the addition of a resin to the fibers before or after the sheet is formed. Papers are not made commercially from metal fibers, and can be made experimentally only in very high weights.[6] The addition of 2 to 10% glass fibers to wood-pulp paper increases its dimensional stability, porosity, and tear strength. Tensile and bursting strength are not affected. Flex endurance is always reduced; 5% glass fiber causes a 50% reduction.[7] Papers containing reinforcing strands of glass filaments are stiff and have very low flex endurance.[6]

A review of the published data on papers containing various synthetic organic fibers alone and in combination with cellulosic fibers indicated that combinations of nylon and wood pulp offered promise for producing papers with desirable properties for the protective garments. Data on the physical properties of nylon-wood pulp papers as determined by Emery and his co-workers[8] are given in Table I-8. The combination of good tensile, tear, and burst strength and the fold endurance of the 50:50 nylon-wood pulp paper made this paper of particular interest for further investigation as a material for the protective overgarment.

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[7] L. L. Warner, TAPPI 42, 173-175 (1959).

[8] J. R. Emery, J. D. Howell, and S. Sands, TAPPI 38, 781-786 (1956).

Table I-8. Properties of Nylon-Wood Pulp Papers[a, b]

% Nylon	Tensile g (15 mm)	Tear, g	Burst, psi/g	Fold, cycles
0	7600	120	19	negligibl
25	500	360	12.5	80,000
50	6200	640	19	160,000
75	6200	1000	24	>160,000
100	6200	1400	25	>160,000

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[a] 3.8 g handsheets, 8 x 8 in.

[b] 22% polyamide binder.

Fold, cycles
negligibl
80,000
160,000
160,000
160,000

b. Survey of commercial papers

Numerous types of papers are produced commercially for use in garments and other applications for which woven or knit fabrics have generally been used in the past, and the properties of these papers have been steadily improved. To determine whether any papers were available at the time this investigation was undertaken, we made a survey of the papers that were being produced in the United States. The known manufacturers of papers for possible use in garments were:

Kimberly-Stevens

Scott Paper

West Virginia Pulp and Paper

St. Regis Paper

Riegel Textile

Mead Paper

Ludlow Paper

Hollingsworth and Vose

Clupak, Inc.

C. H. Dexter and Sons

Enterprise, Inc.

Angelco Uniform

Avondale Industries

Disposables, Inc.

Williamson Dickie, Ace High Division

No-Wet-Thru

Most of these companies were contacted about their products and the majority of them sent samples of products that they produced or information about their products.

(1) Papers selected for evaluation

A review of the information and the samples indicated that the types of paper most used for garments were reinforced papers, laminates, and synthetic fiber papers. Papers representative of these types were selected for evaluation on the basis of the hand, drape, weight, tearing strength, and price. Their properties are given in Table I-9.

Kimberly-Stevens reinforced papers were cellulose reinforced with nonwoven nylon scrim. Kaycel RSR 8514 was similar to Kaycel 101-1 but had a water repellent treatment and was treated to improve abrasion resistance. Kaycel RSR 8525 had a scrim with a higher count than Kaycel 101-1 and Kaycel RSR 8514 and had been treated to improve abrasion resistance. CWC 15-2 contained a special wadding surface and was treated with Rhoplex B-15 and then with FC-208 (fluorocarbon).

The Mosinee[5] product was creped, unbleached kraft paper that was similar to a paper that was reported to be most desirable for disposable fire-fighting clothing.

Chicopee's reinforced paper, Chixel, was a cotton gauze surfaced with cellulose wadding.

Kaycel 100 (polyethylene coated) had the same base material as Kaycel 101-1 but contained a 0.6-mil polyethylene coating. The disposable rain coat fabric of Disposables, Inc., was reported to be a paper treated by a resin process developed by the American Cyanamid Company.[9]

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9. American Textile Reporter 74, 47 (March 10, 1960).

Table I-9. Properties of Commercial Papers

	Weight, oz/yd²	Thickness, mils	Breaking strength, lb/in.				Elongation at break, %				Elmendorf tear, g				Abrasion resistance		Air permeability, ft³/min/ft², 0.5 in. water
			Dry		Wet		Dry		Wet		Machine		Cross				
			Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Range	Average	Range	Average	Cycles	Weight loss, %	
A. Reinforced Papers																	
1. Mosinee creped paper	5.3	46.8	28.6	24.9	7.3	5.9	11.4	4.0	4.6	1.8	1632-2496	2010	1344-1984	1567	>200	1.73	21.0
2. Kaycel 101-1	2.6	7.4	12.8	8.3	9.6	7.5	18.1	19.3	15.9	21.6	352-1696	889	1088-1792	1389	5	2.43	19.3
3. Kaycel 101-3	2.6	8.4	17.4	9.2	10.9	7.7	2.2	1.9	1.6	1.7	796-1696	1254	1568-2624	2189	7	3.25	10.8
4. Kaycel RSR 8525	3.0	10.5	24.0	21.2	16.0	19.2	2.5	2.4	1.8	2.6	1664-2592	2256	a	a	>200	1.48	10.4
5. Kaycel RSR 8514	2.5	9.6	20.5	11.2	11.6	9.0	7.5	4.5	6.2	6.6	2048-2336	2195	1584-2208	1840	200	11.9	16.0
6. Kaycel CWC 15-2	3.1	-	13.8	13.0	10.2	10.2	21.0	18.4	26.3	24.0	-	1043	-	373	206	-	37.0
7. Chixel	2.0	12.1	7.6	5.7	6.6	4.8	5.0	10.0	9.6	13.8	112-192	150	80-128	106	15	1.76	16.4
B. Laminated Papers																	
1. Kaycel 100, polyethylene coated	2.9	8.0	15.9	12.6	10.7	8.4	2.1	1.8	1.7	2.0	896-1792	1267	1408-2304	1933	26	5.11	<0.5
2. Disposable's rain wear	2.8	7.9	6.3	8.7	7.1	8.8	3.8	4.6	3.6	6.7	640-1696	1011	1440-1632	1517	46	3.0	<0.5
3. No-Wet-Thru 7502	2.0	6.6	21.6	25.8	25.1	23.9	4.8	3.3	2.3	18.1	104-139	124	104-136	122	>200	8.6	<0.5
C. Synthetic Fiber Papers																	
1. Masslinn M-840-B	2.0	8.8	25.8	3.7	8.3	1.1	14.4	18.7	35.2	12.1	208-368	269	96-144	125	57	4.86	218
2. Masslinn RI-750-2299	1.7	9.9	9.7	4.6	4.3	2.9	14.8	22.1	20.9	28.6	112-192	150	96-128	106	116	2.9	>450
3. Masslinn M-1300-2110	3.0	17.6	20.8	6.5	11.5	3.1	14.0	23.0	22.0	51.0	496-640	554	128-208	168	44	4.76	277
4. Dacron textryl	2.4	11.5	14.7	14.6	-	-	74.6	68.0	-	-	-	627	-	650	80	-	50
5. Havatex	2.5	12.5	13.4	11.4	-	-	15.0	15.7	-	-	-	285	-	294	154	-	91
D. Miscellaneous Papers																	
1. Flexrope 8235	1.3	4.0	22.7	4.2	b	b	3.0	10.8	b	b	80-160	112	80-240	176	26	1.29	9.1
2. Flexrope 8345	0.8	3.3	10.7	2.6	b	b	3.0	3.0	b	b	80-240	112	80-160	112	200	10.9	32
3. Rotoform	1.9	10.5	11.2	10.2	6.9	6.5	23.0	25.5	26.0	33.0	160-280	224	160-336	253	86	6.48	251
4. Bleached filter crepe paper No. 35	1.3	10.0	5.8	11.9	2.2	4.2	1.6	4.0	2.4	4.0	192-352	323	256-320	307	47	12.2	11.5
5. Wet strength cover stock	1.3	8.0	10.9	19.2	3.9	6.8	2.0	3.9	2.8	4.8	80-192	147	80-256	166	135	11.4	<0.5

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[a] Could not be torn.

[b] Fell apart when wet.

No-Wet-Thru, a Mylar-coated paper, was reported[10] to have these properties:

resistance to wetting by water, solvents, grease, oil, and most solvents

absorbency

good wet and dry tensile and tear strengths

softness and good drape

heat sealability

Typical Masslinn papers prepared from acetate and viscose rayons were selected from Chicopee's line of products.

Kimberly-Stevens makes a number of Dacron papers and their Dacron Textryl was selected for further study because of its excellent handle and drape.

Hollingsworth and Vose uses the Rotoformer for making specialty papers from cellulosic or synthetic fibers having stapel length of up to 1 inch.[11] A synthetic fiber paper and three all-wood pulp papers made by Hollingsworth and Vose were selected for evaluation.

The Flexrope papers[5] were selected for evaluation because they were reported to have an unusual fabric-like hand.

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[10] American Textile Reporter 74, 45 (March 10, 1960).

[11] Conference with Mr. John Vaselow of the Hollingsworth and Vose Company in Birmingham on July 29, 1960.

[redacted]

(2) Properties of laminated and coated papers

The laminated and coated papers were characterized by low air permeability. The abrasion resistance of these papers was considerably lower than for Kaycel RSR-8525 or the Mosinee creped paper. No-Wet-Thru, a Mylar-coated paper, had the best abrasion resistance and breaking strength but the poorest tearing strength of the laminated materials. Since the other laminates contained reinforcing strands of yarn, the low tearing strength of the No-Wet-Thru illustrates the importance of reinforcing agents in improving tearing strength. In general, papers that did not contain reinforcing strands or scrim had low tearing strength.

(3) Properties of reinforced papers

Of the commercial papers tested, Kaycel RSR 8525 had the best physical properties for lightweight clothing. This paper was a 3-oz wood pulp paper reinforced with strands of multifilament nylon and treated to improve abrasion resistance. The paper had excellent tearing strength, good abrasion resistance, and good wet and dry breaking strengths. The U. S. Army Natick Laboratories field evaluated garments prepared from Kaycel RSR 8525 and RSR 8514.[12] The RSR 8514 was said to be the better; three samples showed no failures after four runs over the combat course. Nevertheless, the physical properties of Kaycel RSR 8525 were superior to Kaycel RSR 8514, as shown in Table I-9. Especially noteworthy was greater abrasion resistance of the Kaycel RSR 8525. This difference in abrasion resistance was unexpected since the only apparent difference between the papers was the scrim used for reinforcement. Kaycel RSR 8514 contained a 6 x 5 scrim of 100-denier nylon; Kaycel RSR 8525 contained a 9 x 5 scrim of 100-denier nylon in the machine direction and 210-denier nylon in the cross direction. Kaycel RSR 8525 had better physical properties than the Masslin M-840-B and the Kaycel 101-1 that were field evaluated in garments by the U. S. Army Natick Laboratories and by the Defense Research Chemical Laboratories of Canada. Also, the Kaycel RSR 8525 was superior to the Kaycel CWC-15-2 and to the Mosinee creped paper that was found to be the most desirable paper for use in disposable fire-fighting clothing. The

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[12] Information from Mrs. Mary Darby of the U. S. Army Natick Laboratories.

[redacted]

[redacted]

Mosinee creped paper had very good dry breaking strength, tearing strength, and abrasion resistance, but poor wet strength. The weight of the paper, 5.3 oz/yd^2, was higher than desired. The Kaycel 101-1 and 101-3 had extremely poor abrasion resistance. Chixel, a paper reinforced with cotton gauze, had generally poor physical properties.

(4) Properties of synthetic fiber papers

These papers were not reinforced and consequently had low tearing strengths. The abrasion resistance of the papers were low, about the same as for the polyethylene coated papers. These papers had very high air permeabilities, 91-450 ft^3/min/ft^2; a characteristic of nonwoven fabrics. Papers generally have air permeabilities below 50 ft^3/min/ft^2.

(5) Properties of miscellaneous papers

The rope-fiber papers, the Flexropes, had low abrasion resistance and tearing strength, and little wet strength. Polymer impregnants and reinforcing materials could be used to improve the properties of these papers but it is doubtful that they would retain their characteristic pleasant feel which is their only advantage.

A paper made on a Rotoformer was supplied to us by Hollingsworth and Vose. The Rotoformer is used for making specialty papers from cellulosic or synthetic fibers having a staple length of up to 1 inch. The paper evaluated had a high air permeability similar to nonwoven fabrics, but its tensile properties and abrasion resistance were low. This paper was characterized by nearly the same physical properties in the machine direction as in the cross direction.

c. Conclusions

From these studies it was concluded that in general reinforced papers have better properties than nonreinforced papers. The physical properties of Kaycel RSR 8525 and RSR 8514 were superior to the properties of the other commercial papers evaluated, and the properties of these papers were used a standards for accessing the properties of experimental papers. However, the commercial papers have the disadvantages of poor abrasion resistance, poor snag resistance, and in the case of reinforced papers poor adhesion between the scrim and surfacing layers of the papers.

[redacted]

4. Nonwoven fabrics

A survey of the nonwoven fabrics and clothing produced in the United States was made to determine whether any nonwoven fabrics were available that could be used as the basic material for protective overgarments. On the basis of information from the survey, a number of nonwoven fabrics were selected for further study.

a. Survey of manufacturers

Inquires were sent to about 30 companies in the United States that were known to produce or that we thought might produce woven fabrics, requesting information on and samples of any nonwoven materials that might be useful for overgarments. The responses indicated that, at the time of the survey, no nonwoven fabrics were available that were suitable for use in the overgarment; however, the trend in the industry was apparently toward developing durable nonwoven fabrics that would compete with conventional fabrics on a performance basis. The available nonwoven fabrics offered no price advantage over woven fabrics; for example, the cost per pound of nonwoven fabrics was \$0.76 to \$1.29, compared to about \$0.80 for woven cotton fabric and \$1.30 for knitted cotton fabric. Nevertheless, we investigated the properties of some of the available nonwoven fabrics that appeared to have some characteristics of interest.

b. Properties of selected commercial nonwoven fabrics

Two lightweight nonwoven fabrics from Troy Blanket Mills and five from Pellon Corporation were examined.

One of the fabrics from Troy Blanket Mills contained acetate fibers and the other contained viscose fibers. Neither of these fabrics appeared to contain enough binder for satisfactory bonding, since the fabrics were easily torn apart.

The five nonwoven fabrics from the Pellon Corporation were selected for investigation, primarily on the basis of weight and appearance. The properties of these fabrics were determined and are given in Table I-10. The Pellon nonwoven fabrics had good flexibility, good crease recovery, and a pleasant feel when in contact with the skin. The draping qualities of the materials were inferior to those of woven fabrics and the reinforced

[redacted]

Table I-10. Properties of Commercial Nonwoven Fabrics

Nonwoven Fabric	Weight, oz/yd^2	Thickness, mils	Breaking strength, lb/in.				Elongation at break, %				Elmendorf tear, g				Abrasion Resistance		Air permeability, ft^3/min/ft^2, 0.5 in. water
			Dry		Wet		Dry		Wet		Machine		Cross				
			Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Range	Average	Range	Average	Cycles	Weight loss, %	
Pellon 970W	1.6	7.3	4.8	6.1	2.2	6.3	16.6	21.8	23.0	19.6	756-1640	1129	896-1408	1177	177	0.97	332
Pellon 717W	1.3	8.1	6.8	2.6	3.6	5.6	6.7	8.4	5.9	8.0	368-960	554	320-832	618	97	2.94	325
Pellon 40W	2.1	12.1	7.5	15.2	6.3	6.2	5.6	10.8	16.2	12.4	720-832	758	704-1424	970	200	2.30	239
Pellon 901 Nat	1.6	6.1	4.4	14.1	2.7	8.8	21.3	22.3	34.6	23.7	832-1104	1016	1152-1552	1360	107	0.38	313
Pellon 30W	1.5	8.1	5.6	12.4	3.8	8.0	6.8	2.8	17.0	12.6	336-512	432	240-464	349	155	2.34	288

[redacted]

papers that are used in disposable garments. The air permeabilities of the nonwoven fabrics were high, 288 to 325 ft^3/min/ft^2. The breaking strengths of the fabrics were generally low (2.6 to 15.2 lb/in.) and were especially low in one direction, usually the machine (or warp) direction. In comparisons with the tearing strengths of woven fabrics and reinforced papers, the tearing strengths of the nonwoven fabrics were low. Pellon 40W was the only one of the nonwoven fabrics that was not ruptured after 200 cycles on the Taber Abrader, but it was also the heaviest of the fabrics.

Our survey of the commercially available nonwoven fabrics showed that they were not being produced for outerwear. Nonwovens were available in the desired weight range and they were highly permeable to air and water vapor; but, in general, they had low tensile strength, low tear strength, poor abrasion resistance, and poor drape. The price range was about the same as for woven fabrics.

5. Conclusions

From the survey of commercial films, foams, coated and uncoated woven fabrics, nonwoven fabrics, and papers that might be potentially suitable for preparing lightweight protective overgarments, it was concluded that papers offered the most promising possibilities for construction of inexpensive, lightweight, expendable, overgarments. Papers have the advantages of economy, lightweight, permeability to air and water, and they can be treated to give protection against CW agents. However, the commercially available papers were not satisfactory because of poor abrasion resistance, poor snag resistance, and, in the case of reinforced papers, poor adhesion between the scrim and the surface layers. The development of papers with improvements in these properties appeared feasible and to provide the most promising route to material that would meet the requirements for the overgarment at the time.

Plastic films in general had poor snag resistance, low water vapor permeability, and no air permeability, which precluded their use in the overgarments. The low breaking strength and tearing strengths and poor abrasion resistance of foams made them unsatisfactory for use as unsupported base materials.

Uncoated woven fabrics were expensive and too heavy for use in expendable overgarments and coated woven fabrics were unsuitable because of low tearing strength, poor abrasion resistance, low air permeability, and relatively high cost.

B. Studies to Overcome Deficiencies of Commercial Papers

The review of commercially available papers indicated that, although some had desirable qualities, even the most promising types were deficient in strength and abrasion resistance of papers can be increased by application of certain resins. We, therefore, made trials to compare the effectiveness of different types of resins for improving the properties of one of the most promising papers as indicated by the review described in Section III-A-3.

1. Materials and methods of application

Kaycel 101-1 was used for most of the impregnation studies. Kaycel 101-1, a product of the Kimberly-Clark Corporation, is composed of a nonwoven nylon web between two layers of bleached sulphite wadding. The nylon web is composed of 100-denier multifilament nylon yarn, with 6 strands per inch in one direction and 5 strands per inch in the other. The wadding has been treated to make it fire and water resistant. The paper weighs 3.3 oz/yd^2.

Kaycel 100 was used in one experiment to investigate the usefulness of Geon 577 for imparting both abrasion resistant and flame retardant properties. Kaycel 100 is the same as Kaycel 101-1 except the wadding is not treated to make it water and fire resistant.

The latexes used in the study are described in Table I-11. Suitable dilutions were applied to the papers by padding on a Butterworth laboratory padder. The impregnated papers were dried for 30-40 minutes in circulating air at 120°C.

The first six latexes listed in Table I-11 were chosen for investigation because they were types that were known to be useful for improving the properties of papers and nonwoven fabrics. The Hycar 4501,[13] Chemigum 245 CHS, and FC-805[14] were included because they were reported to be effective for providing resistance to liquid CW agents and they offered possibilities for improving the physical properties of paper simultaneously.

2. Comparison of latexes

The effects of the latex treatments on the physical properties of Kaycel 101-1 are shown in Table I-12.

All of the treatments except that with the combination of Chemigum 245 CHS and FC-805 improved the dry breaking strength of the paper. Rhoplex B-15 and Rhoplex AC-33 produced the greatest improvement in combined machine and cross dry breaking strength.

The treatments resulted in only relatively small, if any, improvement in the wet breaking strength of the paper.

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[13] Reported to Dr. W. C. Sheehan at a conference with Mr. Roberts, Mr. Gilchrist, and Dr. Oglesby of the Chemical Corps in Edgewood on September 15, 1960.

[14] Memorandum to Mr. Guy Schrag, U. S. Army Natick Laboratories, from A. D. Little, Inc., March 15, 1960.

[redacted]

Table I-11. Latexes Used for Impregnation

Trade name	Manufacturer	Description of polymer	Solids, %	Particle size, microns	Minimum film forming temp., °C	Film properties	Oil and grease resistance	Abrasion resistance	Heat sealability
Neoprene 842A	Du Pont	neoprene	50	-	-	soft	good	fair	very poor
Rhoplex B-15	Rohm & Haas	acrylic polymer	46	<1.0	0	soft, transparent	good	very good	good
Rhoplex AC-33	Rohm & Haas	acrylic polymer	46	-	21	soft, transparent	good	good	good
Rhoplex C-72	Rohm & Haas	acrylic polymer	45	0.5	39	hard tough, transparent	good	very good	good
Dow Latex 512K	Dow Chemical	60:40 styrene-butadiene copolymer	48	0.2	a	clear tough, rubbery	-	good	very poor
Hycar 1572	B. F. Goodrich Chemical	carboxy modified butadiene-acrylonitrile copolymer, medium high acrylonitrile content	50	0.14	a	clear, rubbery	excellent	good	good
Hycar 4501	B. F. Goodrich Chemical	acrylic ester	50.4	0.13	-	rubbery	good	good	good
Chemigum 245 CHS	Goodyear	67:33 butadiene-acrylonitrile copolymer	42.5	0.15	-	rubbery	good	good	-
FC-805	Minnesota Mining and Manufacturing	30% solution of the chrome complex of perfluoro-octanoic acid in 95% iso-propanol.	30.0	-	none	-	excellent	-	none
Geon 577	B. F. Goodrich Chemical	vinyl chloride	55.0	-	-	-	good	good	very good

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[a] Film forms at room temperature.

[redacted]

[redacted]

Table I-12. Properties of Kaycel 101-1 Impregnated with Various Latexes

Latex	Latex solids,[a] %	Breaking strength, lb/in.				Elongation at break, %				Elmendorf tear, g				Abrasion resistance		Air permeability, $ft^3/min/ft^2$, 0.5 in. water
		Dry		Wet		Dry		Wet		Machine		Cross				
		Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Range	Average	Range	Average	Cycles	Weight loss, %	
None		12.8	8.3	9.6	7.5	18.1	19.3	15.9	21.6	352-1696	889	1088-1792	1389	5	2.43	19.3
Neoprene 842A	25	14.5	13.3	10.5	9.3	22.8	19.9	17.0	17.3	384-576	467	1920-3104	2426	82	0.73	0.5
Rhoplex B-15	25	14.8	15.3	10.3	9.6	25.2	24.0	16.5	22.4	512-608	557	992-1440	1414	>200	0.64	14.0
Rhoplex AC-33	25	16.8	13.4	10.2	8.4	27.4	17.6	17.7	19.0	480-640	544	1344-1536	1434	>200	0.68	10.8
Rhoplex C-72	25	16.5	11.2	10.6	8.4	21.4	16.7	16.6	17.8	464-608	544	960-2144	1434	>200	7.08	12.0
Dow Latex 512K	25	15.1	12.6	11.9	9.2	24.2	23.6	16.0	20.0	704-1600	1024	1408-2120	1800	189	6.10	13.0
Hycar 1572	25	15.7	12.3	10.3	8.1	26.3	21.6	20.0	20.3	670-1212	557	1440-2304	1414	151	4.97	12.8
Hycar 4501	25	15.2	12.6	9.4	7.0	7.3	6.5	5.4	5.9	576-800	709	1376-1728	1453	32	1.33	19.0
Hycar 4501	40	13.3	11.6	10.0	7.4	6.1	6.6	5.4	5.1	704-992	762	1248-1512	1378	>200	3.39	16.7
Chemigum 245 CHS	25	14.1	11.4	9.0	6.7	17.2	21.2	16.6	19.8		864		2144	>200	14.2	8.9
Chemigum 245 CHS and FC-805	25[b]	12.6	9.4	10.0	8.0	5.8	5.3	5.5	4.2	960-1648	1275	896-1696	1235	>200	8.59	10.3

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[a] Latex solids based on the untreated weight of the sample.

[b] Equal parts of Chemigum 245 CHS and FC-805 solids.

[redacted]

The elongation at break of the dry paper was most improved, and to about the same extent over all, by the treatments with Rhop B-15, Hycar 1572, Dow Latex 512K, Rhoplex AC-33, and Neoprene 842A but they had no significant effect on the elongation at break of the wet paper. The treatments with Hycar 4501 and the Chemigum 2 CHS-FC-208 combination greatly reduced the elongation at break of both wet and dry paper.

The values given for Elmendorf tear strength would indicate that the treatment with Dow Latex 512K was very effective for improving this property; however, the difficulties encountered with slippage of the nylon yarns in the paper when making measurements on this paper makes the result questionable.

All of the treatments greatly improved the abrasion resistance of the paper, as judged by the number of cycles for rupture, but the weight losses varied greatly for the various treatments. Considering both the cycles to rupture and weight loss the treatments with Rhoplex B-15 and Rhoplex AC-33 were the most effective for improving the abrasion resistance of the paper.

Only the treatment with Neoprene 842A seriously affected the air permeability of the paper.

The heat sealability of the paper treated with these various latexes was examined briefly and none of them showed promise in this respect.

Comparisons of flexibility and tackiness of the treated papers at -55°C and 45°C, respectively, are given in Table I-13. These treated with Rhoplex B-15, Rhoplex AC-33, and Hycar 4501 were least affected at both of the extremes of temperature.

None of the latex treatments was effective for making the paper resistant to a liquid CW simulant.

Based on the over-all results, Rhoplex B-15 and Rhoplex AC-33 were the most promising of the latexes evaluated for improving the properties of Kaycel 101-1. There was little choice between the two latexes, but Rhoplex B-15 was selected for more extended studies.

[redacted]

Table I-13. Flexibility and Tackiness of Impregnated Kaycel 101-1 at -55°C and 45°C

Latex	Add-on of latex solids, %	Flexibility, -55°C	Tackiness, 45°C
None	-	fair	none
Neoprene 842A	25	poor, but not brittle	very tacky
Rhoplex B-15	25	fair	none
Rhoplex AC-33	25	fair	none
Rhoplex C-72	25	poor	none
Dow Latex 512K	25	poor and no recovery when bent	very slight
Hycar 1572	25	fair	slight
Hycar 4501	40	fair	none
Chemigum 245 CHS and FC-805	25	poor	none, but stiff

[redacted]

3. Effects of various amounts of Rhoplex B-15 on physical properties of Kaycel 101-1

Samples of Kaycel 101-1 were treated by padding to apply 10, 20, 25, and 40% of resin solids. The treated papers were dried 30-40 minutes at 120°C. The physical properties of the treated and untreated papers are shown in Table I-14.

The treatment to apply 25% of resin was the most generally effective for improving the properties of the paper. This treatment improved the dry and wet breaking strengths, the wet tearing strength, the elongation at break, and the abrasion resistance. The data indicate that the treatment caused a decrease in the dry tearing strength in one direction, but this seems questionable in view of the data for the samples treated to apply 10% and 40% of the resin. The only definite adverse effects of the treatment were a moderate increase in stiffness of the paper and correspondingly slightly poorer draping qualities.

4. Trials with Geon 577

In previously described studies, Rhoplex B-15 and Rhoplex AC-33 were found to be the best of a number of latexes for producing desired qualities in papers for protective overgarments. However, it is difficult to make the paper treated with these resins flame retardant. Therefore, we made additional trials with a poly(vinyl chloride) latex, Geon 577. Vinyl chloride resins have, in general, outstanding flame retardant characteristics. Geon 577 (B. F. Goodrich Chemical Company) is an aqueous dispersion of a vinyl chloride resin along with a non-burning plasticizer.

[redacted]

Table I-14. Properties of Kaycel 101-1 Impregnated with Rhoplex B-15

Add-on, % solids	Breaking strength, lb/in.				Elongation at break, %				Elmendorf tear, g				Abrasion resistance		Stiffness, mg	Drape	Flexibility at -55°C	Tackiness at 45°C
	Dry		Wet		Dry		Wet		Dry		Wet							
	Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Cycles	Weight loss, %				
None	12.8	8.3	9.6	7.5	18.1	19.3	15.9	21.6	889	1389	871	768	5	2.43	10	good	fair	none
10	14.6	10.9	8.9	7.1	19.4	19.6	18.3	20.2	827	1400	1288	2215	78	4.5	44	fair	fair	none
20	15.7	13.3	10.0	7.6	20.9	22.0	19.8	18.8	554	1138	1588	1981	200	5.5	44	fair	fair	none
25	14.8	15.3	10.3	9.6	25.2	24.0	16.5	22.4	557	1414	1244	1344	200	0.64	44	fair	fair	none
40	12.5	9.5	7.6	7.6	21.0	20.1	16.7	18.5	856	1283	2458	2663	200	2.6	44	fair	fair	none

[redacted]

[redacted]

Kaycel 100 was treated with Geon 577 to apply 25% solids. On evaluation for abrasion resistance, the treated paper ruptured at 16 cycles. A comparable sample treated with Rhoplex B-15 withstood over 200 cycles. In attempts to improve the abrasion characteristics of Geon 577, it was used in different ratios with other latexes, but the abrasion resistance values for treated papers were not increased enough to be of interest.

In another comparison, samples of Kaycel 101-1 were treated by impregnation to apply 25% solids of Geon 577 and of Rhoplex B-15. The properties of the two treated papers are given in Table I-15. The Geon 577-bonded paper was poorer in all properties except tear strength and air permeability.

5. Conclusions

From the results of these studies of the effects of resin treatments on the properties of papers, it was concluded that it should be possible to develop a paper with physical properties that would meet most of the requirements for a material for the expendable protective overgarment, as described in Section III-A. A paper composed of two surface layers reinforce with a nonwoven scrim and containing about 25% of an acrylic resin offered a promising starting point for the development of a satisfactory paper for the overgarment.

[redacted]

[redacted]

Table I-15. *Physical Properties of Kaycel 101-1 Impregnated with Geon 577 and Rhoplex B-15*

Latex[a]	Breaking strength, lb/in.				Elongation at break, %				Elmendorf tear, g		Abrasion resistance		Air permeability, ft³/min/ft², 0.5 in. water
	Dry		Wet		Dry		Wet						
	Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Machine	Cross	Cycles	Weight loss, %	
Rhoplex B-15	14.8	15.3	10.3	9.6	25.2	24.0	16.5	22.4	557	1414	200	0.6	14.0
Geon 577	12.4	9.7	8.8	5.7	15.9	18.6	13.6	17.1	1354	2464	200	25.3	17.0

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[a] Papers contain 25% latex solids on the weight of the fiber.

[redacted]

C. Experimental Paper Materials

The early studies of various commercially available materials for the expendable protective overgarment indicated that papers were promising because they offered combination of lightweight, permeability to air and water vapor, ease in making them resistant to liquids, and low cost relative to many other materials. However, the physical properties of the papers in commercial production were not satisfactory for the requirements for the overgarments, and studies were undertaken to determine whether the desired properties could be obtained by suitable choice of fibers, use of binders, and reinforcing with yarns.

The terms nonreinforced and reinforced, respectively, are used in this report to distinguish between products formed directly by the paper-making screen (even though they might contain special types of fibers to provide extra strength) and products made by bonding one or more layers of a paper to another material, such as yarn, scrim, nonwoven fabric, or woven fabric.

1. Nonreinforced papers

Nonreinforced papers were made containing 10 different fibers alone and in various combinations. The usual procedure for preparing experimental papers was as follows: The fibers were beaten or slurried with water; if mixed fiber sheets were to be made, the slurries were mixed in the desired proportions; 8 x 8 inch handsheets were formed on a laboratory mold and pressed and dried; and the sheets were treated to apply 25 or 30% of a resin binder. Wood-pulp fiber was used in many of the papers because of its desirable general properties, its good paper-making qualities, and its low cost.

a. Wood-pulp papers

In the studies of all-wood-pulp papers, two types of kraft pulp, bleached and unbleached, were used. The effects of beating time (freeness), of treatments with different resin binders, and of addition of the binders to the furnish or the sheet on the properties of wood-pulp papers were investigated.

[redacted]

Bleached and unbleached Southern-pine kraft pulps obtained from International Paper Company were used in these experiments. One-pound samples of the pulps were beaten for various times with 23 liters of water in a Valley laboratory beater and freeness of each sample was determined. Portions of the beaten pulp slurries were diluted with water to make a slurry containing 0.5% of dry pulp and each slurry was stirred for 90 minutes before use.

The handsheets were formed in a Williamson 8 x 8-in. sheet mold with a 100-mesh stainless steel screen. For each handsheet, about 3 liters of water was put in the mold, then an amount of fiber slurry containing 3.5 g ±0.2 g of dry fiber was poured into the mold. The slurry was stirred thoroughly, but gently to prevent foaming, with a perforated plate agitator. The waterleaf was then formed by applying suction to remove the water. The waterleaf was removed from the screen on a blotter, and pressed between blotters for 1 to 2 minutes at 200 psi pressure, then dried on an electric dryer for 10 to 15 minutes at 120°C. The blotters and the 100 mesh screen were sprayed with ReleasaGen before use to prevent sticking of the waterleaf. Ten to 15 replicate handsheets were made from each slurry. They were conditioned for a minimum of 24 hours in an atmosphere at 21°C and 65% RH before making measurements of physical properties.

The results of measurements of tear strength, air permeability, stiffness, and brusting strength are given in Table I-16.

To obtain satisfactory formation of the handsheets, it was necessary to beat the bleached pulp to a Canadian freeness of at least 760 and the unbleached pulp to a freeness of at least 840. As beating time was increased and the freeness of the pulps was decreased, tearing strength, air permeability, hand, and stiffness of the papers, in general, decreased slightly. Bursting strength, however, increased with increasing beating time. There were only minor differences between the properties of the unbleached papers and the bleached papers.

The papers made from the bleached pulp that had been beaten to a freeness of 760 had the highest tearing strength and air permeability. The papers made from the bleached pulp that had been beaten to a freeness of 435 had the highest bursting strength and the lowest stiffness. All of these 100% wood pulp papers had low air permeabilities and poor handle.

[redacted]

Table I-16. Properties of 100% Wood-Pulp Papers[a] Prepared from Pulps Beaten for Different Times

Beating time, min	Canadian standard freeness, ml	Elmendorf tear, g	Air permeability, $ft^3/min/ft^2$, 0.5 in. water	Stiffness, mg	Bursting strength, psi
Unbleached pulp					
60	840	170	0.8	347	48
90	600	169	<0.5	428[b]	54
120	470	173	<0.5	247	56
160	435	160	<0.5	262	59
Bleached pulp					
50	760	176	1.0	393	53
80	640	172	<0.5	375	56
110	575	169	<0.5	253	62
150	435	134	<0.5	213	64

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[a] 3.5 g handsheets.

[b] Average of 10 determinations made on several samples.

[redacted]

It appeared that papers made from wood-pulp fiber alone were not suitable for use in garments. Even though flexibility, handle, and drape might have been obtained by creping, no method was available for increasing the air permability of the papers to a suitable level.

b. Cotton-linters papers

Handsheets weighing 3.5 g were made from first-cut cotton linters beaten to a freeness of 600, 175, and 75 Canadian Standard. Data on the physical properties of the papers are given in Table I-17. As the beating time of the cotton linters was increased, the tearing strength, hand, and stiffness decreased. However, the bursting strength increased with increasing beating time. The air permeability of the papers was low and they had poor drape.

It was concluded that paper made from cotton linters alone was not suitable for use in the overgarment because of low air permeability, stiffness, and poor drape.

c. RD-101 papers

RD-101 is a multi-cell rayon fiber made by American Viscose Corporation especially for use in paper. The fiber used was 1.5-denier, 0.25 in. staple.

Shearer[15] reported that in order to reduce the level of overlength and chip fibers which may be present it was sometimes necessary to beat RD-101 fibers for a short time. Therefore, handsheets were made from RD-101 fibers as received from the manufacturer and from fibers that had been beaten for 30 minutes. The slurries of both the unbeaten and the beaten fibers were stirred for 90 minutes before use. The values of tearing strength, air permeability, stiffness, and bursting strength of 3.5 g handsheets of these papers are given in Table I-17.

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[15] Howard E. Shearer, Paper Trade J. 144, 42-43 (November 7, 1960).

b Average of 10 determinations made on sev al samples.

[redacted]

[redacted]

Table I-17. Properties of 100% Cotton-Linters Papers and RD 101 Papers

Fiber	Beating time, min	Canadian Standard freeness, ml	Elmendorf tear, g	Air permeability, $ft^3/min/ft^2$, 0.5 in. water	Stiffness, mg	Bursting strength, psi
Cotton linters		600	147	<0.5	226	26
		175	137	<0.5	173	36
		75	90	<0.5	164	54
RD-101	0	-	125	<0.5	289	26
	30	-	122	<0.5	284	31

[redacted]

[redacted]

Beating for 30 minutes decreased slightly the tearing strength and the stiffness of papers made from RD-101 fibers. As with other papers, there was a slight increase in the bursting strength with increased beating time. These papers had poor drape and low air permeability.

d. RD-101-rayon papers

The rayon fiber used in these trials was 1.5-denier, 0.25-in. staple XL rayon. Slurries for making handsheets were prepared by adding required amounts of RD-101 and XL rayon fibers directly to the total amount of water required to make 0.4% slurries, and stirring the slurries 90 minutes before use. Approximately 3.5 g handsheets were made.

The physical properties of papers containing blends of rayon and RD-101 fibers are given in Table I-18. The breaking strength and tearing strength of the paper containing 50% RD-101 and 50% rayon as well as paper containing 75% rayon and 25% RD-101 were extremely poor and thus the paper would be unsuitable for use in overgarments.

e. All-nylon and nylon-wood pulp papers

The nylon fiber used in these trials was 0.25 in. staple, 1.5 denier. Preliminary trials showed that it was necessary to have some bonding resin in the handsheets containing nylon fibers when they were formed in order to facilitate handling them. A slurry for making handsheets was prepared by dispersing 60 g of the nylon fiber in 11.3 liters of water containing 0.016% of Santomerse SX. After stirring the slurry for 30 minutes with a motor-driven propellor, 5.4% by weight of Rhoplex B-15, which contained 46% solids, was added and stirring was continued for 1 hour. Foaming was controlled during stirring by the addition of small amounts of Antifoam A as required. The final slurry contained 0.5% nylon, 0.015% Santomerse SX, 2.5% Rhoplex B-15 solids, and a small amount of Antifoam A.

[redacted]

[redacted]

Table I-18. Physical Properties of Rayon-RD-101 Papers

Fiber content	Weight, oz/yd^2	Thickness, mils	Breaking strength, lb/in.	Elmendorf tear, g	Air permeability, ft^3/min/ft^2, 0.5 in. water	Stiffness, mg	Drape	Handle
50% Rayon 50% RD-101	2.5	16.2	2.0	30	16	46	fair	good
75% Rayon 25% RD-101	2.4	17.4	0.41	22	103	38	fair	good

[redacted]

[redacted]

The wood-pulp slurry was prepared by heating bleached kraft pulp to a freeness of 600 Canadian Standard. Twenty-three liters of water was put into the beater and one pound of the dry pulp, torn into small pieces, was added. The pulp was dispersed by running the beater for a few minutes without any weight on the lever arm of the bed plate. A 5500-g weight was then hung on the lever arm of the beater, and the pulp was beaten to obtain the desired freeness. The time for obtaining the desired freeness, about 70 minutes, was very reproducible. Portions of the beater slurry were diluted with water to give a pulp content of 0.5%. Rhoplex B-15 was added to the beater slurry and the mixture was diluted to give a slurry containing 0.5% wood pulp and 2.5% Rhoplex B-15 solids. All diluted slurries were stirred 90 minutes before use.

Handsheets containing 3.5 ±0.2 g of dry fiber was made containing 100% wood-pulp fiber and mixtures of wood-pulp fiber and nylon fiber in ratios of 75:25, 50:50, and 25:75 by the procedure described above for preparing wood-pulp papers.

After drying, the handsheets were bonded with Rhoplex B-15. The latex was applied by placing a dry handsheet between two 60-mesh stainless steel screens, and then dipping the sheet into an aqueous dispersion of the resin. The impregnated sheet, still between the screens, was pressed between blotters in a hydraulic press to leave a pick-up of approximately 30% of B-15 solids based on the dry fiber weight. The screens were then removed, and the sheet was dried in circulating air at 120°C for 30-40 minutes. The 100% wood-pulp sheets were impregnated with a dispersion containing 20% Rhoplex B-15 solids; the sheets containing nylon were impregnated with a dispersion containing 15% Rhoplex B-15 solids.

The physical properties of the papers so prepared are given in Table I-19. As the nylon content of the papers increased, dry and wet breaking strengths decreased; elongation, tearing strength, and air permeability increased. The presence of 25% nylon in the paper appreciably improved its abrasion resistance. Papers containing 50% nylon had slightly lower abrasion resistance than the 25% nylon papers. Abrasion resistance decreased sharply as the nylon content of the paper was increased above 50%.

[redacted]

Table I-19. Physical Properties of Papers Containing Various Synthetic Fibers in Combinations with Wood Pulp

Fiber content	Weight, oz/yd²	Thickness, mils	Breaking strength, lb/in. Dry	Breaking strength, lb/in. Wet	Elongation, at break, % Dry	Elongation, at break, % Wet	Elmendorf tear, g	Abrasion resistance Cycles	Abrasion resistance Weight loss, %	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg	Bursting strength, psi	Drape	Handle
100% Wood pulp[a]		5.4	35.8	15.9	3.0	10.6	147	290	5.55	0.5				
75% Wood pulp[a] 25% Nylon		8.9	28.2	15.9	6.1	13.8	266	200	1.15	32.0				
50% Wood pulp[a] 50% Nylon		8.2	23.5	9.0	14.2	13.2	604	200	1.35	32.1	133		poor	slightly boardy
25% Wood pulp[a] 75% Nylon		14.2	11.6	5.8	16.6	14.0	842	200	4.20	35.0				
100% Nylon[a]		16.3	9.1	3.9	10.8	10.0	1066	108	1.09	253.0				
75% Wood pulp[a] 25% Poly(vinyl alcohol)		9.2	35.3	21.6	5.9	13.0	253	200	4.29	0.8				
50% Wood pulp[a] 50% Poly(vinyl alcohol)		9.3	31.8	11.9	8.2	11.5	306	200	0.90	2.8				
25% Wood pulp[a] 75% Poly(vinyl alcohol)		10.3	22.2	13.7	10.3	13.6	314	200	2.83	17.5				
100% Poly(vinyl alcohol)[a]		17.2	13.7	9.5	11.5	12.6	345	103	5.63	73.0				
50% Wood pulp[a] 50% Cellulose acetate	3.3	7.6	14.3	8.5	1.5	2.6	195	137	1.20	7.5	134		poor	boardy
50% Wood pulp[a] 25% Cellulose acetate 25% Nylon	3.3	10.7	10.7	6.2	1.7	3.2	394	136	0.44	30.5	89		poor	boardy
25% Wood pulp[b] 75% Dacron	3.3		11		20		1080	151	rupture	134	84	47	good	soft
50% Wood pulp[b] 50% Dacron	3.4		19		10		602	200	5.1	24	122	43	poor	fair
75% Wood pulp[b] 25% Dacron D-90	3.3		31		6		336	200	0.7	<0.5	218 218	73	very poor	boardy
50% Wood pulp[b] 50% Dacron D-90	3.4	12.3	15.1		8.6		508	145	2.2	30	390		poor	poor
25% Wood pulp[b] 75% Dacron D-90	3.4	18.9	11.8		9.2		580	92	6.1	92	173		poor	poor
75% Wood pulp[b] 25% Polypropylene	3.4	14.0	17.0		7.6		93	200	5.7	13	58		poor	poor

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[a] Papers contained 30% Rhoplex B-15 solids on the weight of the fiber.

[b] Papers contained 25% Rhoplex B-15 solids on the weight of the fiber.

The papers containing 50% nylon had the best balance of physical properties. The tear strength and abrasion resistance of this paper were greater than that of the commercial synthetic fiber papers that were tested; air permeability was lower; breaking strength was about the same. The abrasion resistance of the paper containing 50% nylon was slightly greater than the abrasion resistance of Kaycel RSR-8525, the best of the commercial papers. However, Kaycel RSR-8525 had higher dry and wet breaking strengths and tearing strengths (Table I-9) which were probably due to the reinforcing scrim.

f. All-poly(vinyl alcohol) and poly(vinyl alcohol)-wood pulp papers

The poly(vinyl alcohol) fibers used in these experiments were $\frac{1}{8}$-inch, 1.0-denier Vinal fibers. A slurry containing 0.5% of the Vinal fibers and 0.015% of Santomerse SX was prepared as described for the nylon fibers. The wood-pulp slurry was prepared as previously described by beating bleach kraft wood pulp to a freeness of 600 and diluting it with water to make an 0.5% slurry. No latex was added to these slurries.

Handsheets (3.5 g) were prepared as previously described from the slurry of the Vinal fibers and from mixtures of Vinal and wood-pulp slurries to provide wood-pulp: Vinal ratios of 75:25, 50:50, and 25:75. The handsheets were treated, as previously described, to apply approximately 30% Rhoplex B-15 solids.

The physical properties of these papers are given in Table I-19. The breaking strengths of the papers prepared from poly(vinyl alcohol) fiber and wood pulp fiber mixtures were superior to the nylon-wood pulp papers as shown in Table I-19. The breaking strength of the papers containing poly(vinyl alcohol) fiber decreased with increasing amounts of poly(vinyl alcohol); tear strength and air permeability increased with increasing amounts of poly(vinyl alcohol). Poly(vinyl alcohol) was not as effective as nylon for improving the abrasion resistance and tearing strength. For example, the weight loss due to abrasion for papers containing 50% nylon was 1.35%, compared to 6.9% for the papers containing 50% poly(vinyl alcohol). The addition of 50% poly(vinyl alcohol) increased the tear strength 140%, compared to an increase of 371% with the use of 50% nylon. The air permeabilities of the papers containing poly(vinyl alcohol) were much lower for all samples than the air permeabilities of the papers containing nylon. Low tearing strength, poor abrasion resistance, and low air permeability do not encourage any further work with papers prepared from poly(vinyl alcohol)-wood pulp blends.

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[a] Papers contained 30% Rhoplex B-15 solids on the weight of the fiber.

[b] Papers contained 25% Rhoplex B-15 solids on the weight of the fiber.

g. Cellulose acetate-wood pulp papers

Since cellulose acetate fibers have some absorptive power for VX agent, a study was made on the properties of papers containing the fiber along with wood pulp. The cellulose acetate used in these experiments was 0.25-in. staple, 2.5-denier fiber obtained from Celanese Fibers Company.

We were unable to prepare paper handsheets with 100% cellulose acetate fiber because of the very low wet strength of the waterleaf. The addition of a binder to the beaten stock did not alleviate this problem. However, no difficulty was experienced in preparing papers containing 50% or more wood pulp. The procedures for preparing the fiber slurries and the handsheets and for applying the resin binder were the same as described for preparing the wood pulp-Vinal papers in Section c above. The handsheets were made to contain 3.5 g of dry fiber.

The data on the physical properties of this paper are given in Table I-19. In comparison with a 100% wood-pulp paper that also contained 30% binder, the cellulose acetate-wood pulp paper had lower dry and wet breaking strength, lower elongation, and lower abrasion resistance. It had higher tearing strength and higher air permeability. The drape and handle of the paper containing cellulose acetate was slightly better than the all wood-pulp paper.

Handsheets also were made containing 25% nylon, 25% cellulose acetate, and 50% wood pulp to determine if the nylon would improve the physical properties of paper containing cellulose acetate. Also, it was hoped that this combination of fibers would give papers with good drape. The physical properties of this paper are given in Table I-19. The 25:25:50 paper had lower breaking strengths, considerably higher tearing strength and air permeability, and higher abrasion resistance, than the paper containing equal parts of cellulose acetate and wood pulp. The stiffness of the paper containing the nylon was less than the stiffness of the paper without nylon but it was much stiffer than the Kaycels. The drape and hand of the paper was only slightly improved by the nylon and was poor compared to the Kaycels.

Because of the generally poor physical properties, the papers containing cellulose acetate did not appear to be suitable for the purpose of this project.

h. Dacron-wood pulp papers

Dacron fibers have good resistance to heat, high strength, and good flex resistance. Also, commercial papers and nonwovens containing Dacron fibers appear to be more prevalent than other synthetic fiber papers. Therefore, experimental papers containing mixtures of Dacron and wood pulp were made and evaluated for our end use.

Dacron-wood pulp papers were made from two types of Dacron: one type was 1. 5-denier, 0. 25 in. staple of ordinary Dacron; the other was Dacron D-90, a polyester fiber that crimps on heating.

Slurries containing 0. 5% of the Dacron fibers and 0. 5% of bleached wood pulp were prepared as described for the Vinal fiber and wood pulp, respectively, in section c above.

(1) Dacron-wood pulp

Handsheets were made from the slurries of ordinary Dacron and wood pulp to contain these fibers in ratios of 75:25 and 50:50. They were aftertreated with Rhoplex B-15 to apply 30% resin on dry-fiber weight.

The physical properties of the papers are given in Table I-19. The paper containing 50% Dacron and 50% wood pulp had better breaking strength and abrasion resistance than the paper containing 75% Dacron and 25% wood pulp. However, the paper containing 75% Dacron had higher tearing strength and air permeability. Both papers had poor hand and drape. The breaking strength, tearing strength, abrasion resistance, and flexibility of the Dacron-wood pulp paper were poor relative to the properties of the 50% nylon and 50% wood pulp paper.

The low breaking and tearing strengths, poor drape, and low abrasion resistance of the Dacron-wood pulp papers made them of no further interest for the overgarment.

(2) Dacron D-90-wood pulp

Dacron D-90, a polyester fiber that crimps on heating, was investigated in attempts to prepare papers with good hand and drape that would be suitable as a base material for the protective overgarment.

Handsheets containing Dacron D-90 and bleached wood pulp in ratios 25:75, 50:50, 75:25 were prepared from 0.5% slurries of the fibers. The handsheets were aftertreated to apply 30% of Rhoplex B-15 solids on the dry-fiber weight. The properties of the papers are given in Table I-19. As the ratio of Dacron D-90 to wood pulp in the paper was increased from 25:75 to 75:25, the breaking strength, abrasion resistance, and stiffness of the paper decreased; elongation at break, tearing strength, and air permeability increased; and hand and drape improved. The brusting strength of the 50:50 and 75:25 Dacron-wood pulp papers were about the same but were considerably lower than for the 25:75 Dacron-wood pulp paper.

The hand, drape, and flexibility of the 75:25 Dacron D-90-wood pulp paper were much superior to the hand, drape, and flexibility of the 50:50 nylon-wood pulp paper, or to the properties of other experimental papers that we have made. However, the abrasion resistance and breaking strength of the 75:25 paper were low. The 25:75 and 50:50 Dacron-wood pulp papers did not possess outstanding hand and drape. The hand, drape, and flexibility of the 50:50 Dacron-wood pulp paper was about the same as for the 50:50 nylon-wood pulp paper, but the physical properties of the Dacron containing papers were not as good as those of the nylon paper.

i. All-polypropylene and polypropylene-wood pulp papers

The good oil and water resistance of polypropylene made it of interest for trials in papers for the protective overgarment.

Attempts were made to prepare 100% polypropylene papers from 2-denier, 0.25-in. polypropylene staple. It was difficult to disperse the fibers in water, even at 0.2% fiber concentration. The all-polypropylene waterleafs had very low wet strength which was not improved by the addition of small amounts of a binder to the furnish. Drying of the handsheets at 120°C shrank the fibers, and the papers were very stiff and had poor drape and handle.

[redacted]

Only one paper containing polypropylene was evaluated because it was difficult to make a uniform handsheet that contained more than 25% polypropylene. The procedure used for preparing a slurry of the polypropylene fiber was to first disperse 15 g of fiber in a small amount of water in a Waring Blendor and then dilute it to make about 9 liters of slurry. The wood-pulp slurry was prepared as usual. The procedures for making handsheets and treating with Rhoplex B-15 were as described previously.

Table I-19 contains data on the properties of 25% polypropylene and 75% wood pulp paper. The breaking and tearing strengths and abrasion resistance of the polypropylene paper were all poor compared to the properties of 50% nylon and 50% wood pulp paper. The hand and drape of these papers were also poor. The generally poor properties of the polypropylene paper make it unsuitable for use in overgarments.

j. Nylon fibrid-bonded papers

Fibrids have been developed for use in papermaking to provide better bonding of synthetic fibers that cannot be fibrillated as readily as cellulosic fibers. The use of fibrids in paper for the overgarment [illegible] offered a possible means of eliminating the need for a latex binder, thus making possible improvement in handle, reduction in weight, and greater ease of flameproofing.

Nylon fibrid 101, made by E. I. du Pont de Nemours and Company, was investigated in wood-pulp and wood pulp-nylon papers. It is a fibrous synthetic polymer supplied as a damp cake containing 20% solids. The compositions and properties are given in Table I-20. The properties of a 50% nylon-50% wood-pulp paper bonded with Rhoplex B-15 are also given for comparison.

In preparing these papers, the nylon fibrid was dispersed in a small amount of water, and then added to slurries of the nylon or wood pulp. The slurries of the nylon and beaten wood-pulp fibers were prepared as previously described. Handsheets were made and evaluated by the usual procedures.

Table I-20. Properties of Papers with Fibrids as Binders

Type of paper	Weight, oz/yd²	Thickness, mils	Breaking strength, lb/in.	Elongation, at break, %	Elmendorf tear, g	Abrasion resistance, % wt loss after 200 cycles	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg	Drape	Handle
70% Wood pulp 30% Nylon fibrid 101	2.5	8.5	26.3	3.3	125	4.3	<0.5	135	poor	poor
50% Wood pulp 50% Nylon fibrid 101[a]	2.5	8.4	21.8	6.6	224	4.5	3	295	poor	poor
50% Wood pulp 50% Nylon fibrid 101[b]	2.4	10.1	24.5	5.6	150	5.2	9	293	poor	poor
50% Wood pulp[c] 50% Nylon	3.3	8.2	22.8	9.0	694	1.45	32	132	poor	slightly boardy

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[a] Paper cured in press at 200°C for 5 minutes at 50 psi.

[b] Paper cured in oven at 200°C for 10 minutes at no pressure.

[c] Paper contains 25% *Rhoplex B-15 solids on weight of paper.*

The paper containing 70% wood pulp and 30% nylon fibrid binders had a slightly higher breaking strength, but the tearing strength, abrasion resistance, air permeability, and hand were poor relative to the properties of the 50% nylon-50% wood pulp paper. It was concluded that the wood pulp-fibrid was unsuitable for our use.

Two papers containing 50% wood pulp, 30% nylon, and 20% nylon fibrid were made and evaluated. One paper was made by heat fusing the fibrid in a press at 50 psi; the other was made by heat fusing the binder in a circulating air oven without pressure in an attempt to try to improve the drape and handle of the paper. The paper which was fused under pressure had slightly higher tearing strength than the paper heated without pressure. The air permeability was higher for the paper dried without pressure. There were no significant differences between any of the other properties of the two papers.

The breaking strengths of the wood pulp-nylon-fibrid papers were about the same as the breaking strengths of the 50% nylon-50% wood pulp paper, but the tearing strengths, abrasion resistances, and flexibilities were poorer.

Low tearing strength and air permeability and poor handle and drape preclude the use of wood pulp-nylon fibrid papers in the overgarment.

2. Reinforced papers

Reinforced papers were prepared by bonding papers to scrims, textryls, nonwoven fabrics, and woven fabrics.

a. Wood-pulp paper

Initial comparisons of various scrims and adhesives were made with all wood-pulp paper. The paper was made from bleached kraft pulp by the procedure described in Section III-C-1-a.

(1) Scrim-reinforced paper

(a) Comparisons of scrims

Scrims of different constructions and made of various synthetic yarns were compared as reinforcements for wood-pulp paper. The yarns used in the scrims were:

Cellulose acetate: 100-denier, 40-filament, 2-Z twist, Type 4W dull made by Celanese Fibers Company.

Rayon: 100-denier, 60-filament, 2-Z twist, Type 11 dull made by Celanese Fibers Company.

Nylon: 100-denier, 34-filament, 0.5-Z twist, Type 680, made by E. I. du Pont de Nemours and Company, Inc.

Nylon: 200-denier, 34-filament, 0.75-Z twist, Type 300 nylon made by E. I. du Pont de Nemours and Company, Inc.

Nonwoven scrims of these yarns containing 4 x 4, 6 x 6, or 8 x 8 strands of yarn per inch were prepared on a 10 x 10 inch pin frame that was designed to fit over the bottom section of the mold used for making handsheets. In making a reinforced handsheet, in this series of experiments, a 2.0-gram waterleaf of the bleached kraft pulp was formed on the screen of the mold, and the pin frame with the scrim was placed on the mold so that only the scrim touched the waterleaf. A duplicate waterleaf that had been made previously and removed from the screen was placed on top of the scrim and pressed with a roller. The yarns were then cut from the frame. The sandwich was pressed between blotters for 1 to 2 minutes at 200 psi pressure, and then dried for 10 to 15 minutes at 120°C. The reinforced papers were bonded by impregnation with Rhoplex B-[illegible] by the procedure described in Section III-C-1-b. One sample was made with the yarns of this scrim at an angle of 45° to the edges of the handsheet; all others were made with the yarns parallel to the edges.

Data on the properties of these scrim-reinforced papers are given in Table I-21.

Comparisons of the wood-pulp papers containing 4 x 4 strands per inch of the 100-denier cellulose acetate, nylon, or rayon yarns indicated that the reinforcements increased the weight, thickness, dry and wet breaking strengths, tearing strength, abrasion resistance, and crease recovery of the paper. Nylon gave the greatest improvement in properties; rayon the least. Cellulose acetate gave the greatest increase in tearing strength, but only slightly increased wet breaking strength and crease recovery. Rayon significantly improved abrasion resistance and crease recovery but increased breaking and tearing strengths only moderately. Nylon gave the greatest increase in dry and wet breaking strengths, abrasion resistance, and crease recovery, and appreciably increased the tearing strength.

[redacted]

Table I-21. Properties of Wood-Pulp Papers with Scrim Reinforcement[a]

Reinforcement	Strands per in.	Thickness, mils	Weight, oz/yd²	Breaking strength, lb/in. Dry	Breaking strength, lb/in. Wet	Elongation, at break, % Dry	Elongation, at break, % Wet	Elmendorf tear, g	Abrasion resistance Cycles	Abrasion resistance Weight loss, %	Air permeability, ft³/min/ft², 0.5 in. water	Crease recovery, %	Peel strength, lb/in.
None		7.8	3.6	35.4	15.1	3.0	4.0	198	200	1.01	<0.5	20.7	-
Cellulose acetate (100 denier)	4 x 4	9.8	4.0	41.8	17.5	3.4	4.7	504	200	0.58	<0.5	24.2	0.93
Rayon (100 denier)	4 x 4	10.7	4.0	35.7	20.4	3.9	5.4	244	200	0.49	<0.5	32.2	1.10
Nylon (100 denier)	4 x 4	10.2	4.0	49.4	23.2	-	4.7	460	200	0.25	<0.5	33.3	1.70
Nylon (100 denier)	6 x 6	10.2	4.1	50.4[b]	27.8[b]	8.3	13.0	1030	200	0.65	<0.5	50.3	1.56
Nylon (100 denier)[c]	6 x 6	10.2	4.1	46.0[b]	49.2[b]	6.6	10.0	723	200	0.65	<0.5	50.3	1.56
Nylon (100 denier)	8 x 8	10.1	4.3	45.9	27.9	3.4	4.3	747	200	0.88	<0.5	42.0	1.58
Nylon (210 denier)	4 x 4	10.3	4.1	51.0[b]	25.7[b]	8.3	13.0	1122	200	3.35	<0.5	39.6	0.95
Cotton sheeting		13.1	4.0	46.5[b]	59.0[b]	-	-	1658	200	0.67	117	-	-

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[a] Paper contained 25% Rhoplex B-15 solids on weight of paper plus scrim.

[b] Determined on J-2 Model Scott Tester; other values on IP-4 Scott Tester.

[c] Yarns at an angle of 45° to the edges of handsheet.

[redacted]

The maximum values of breaking and tearing strengths and crease recovery were obtained for the paper reinforced with the 100-denier nylon with 6 x 6 strands per inch. The strands of nylon were not as equally spaced in the paper containing 8 x 8 strands per inch as they were in the other papers, and this could have contributed to the low tensile properties of the paper. Flat abrasion resistance decreased as the size of the yarn and the number of strands per inch were increased. The size of the yarn affected abrasion resistance more than the number of strands. For example, when the strands per inch were increased from 4 x 4 to 8 x 8, abrasion resistance decreased from 0.49% weight loss after 200 abrasive cycles to 0.88%, and when the size of the yarn was increased from 100 denier to 210 denier in the 4 x 4 construction, the abrasion resistance decreased from 0.49% weight loss after 200 abrasive cycles to 3.35%. The size and number of yarns apparently influence abrasion resistance by controlling the height and frequency that the surface layer of paper is raised from the center plane. Improved abrasion resistance obtained by the use of reinforcing yarns probably is a result of the dimensional stability that the yarns impart to the paper.

Paper that contained 4 x 4 strands per inch of 210-denier nylon had greater breaking and tearing strength than the paper that contained 4 x 4 strands per inch of 100-denier nylon. The paper containing 6 x 6 strands per inch of 100-denier nylon was the best paper prepared.

It was reported by a paper manufacturer that some properties of reinforced papers are improved when the reinforcing yarns are at a 45° angle with the length of the sheet. It was doubtful that sheets made in the laboratory would show any differences except those that might be realized by cutting test specimens at a 45° angle; nevertheless, we made papers as previously described but with the yarns in the scrim at this angle. The scrim was a 6 x 6 mesh of 100-denier nylon. Test specimens for breaking and tearing strength tests were cut so the yarns were at 45° angles to the edges. The breaking strength of these specimens was 8% less, and the tearing strength was 30% less than for specimens from comparable papers with the yarns parallel to the edges. Abrasion resistance and crease recovery were unaffected by the angle of the yarn in the test specimens. Although the angle of the reinforcing yarns may have an effect on the properties of paper made in machine production, we do not believe this can be demonstrated under laboratory paper-making conditions.

Inspection of commercial reinforced papers after they had been field-evaluated showed that the surface layer was frequently loosened in small areas. This deficiency was believed to be due to low peel strength, the strength required to separate the layers of a reinforced paper.

The peel strengths for the experimental reinforced papers ranged from 0.93 to 1.7 lb/in. The peel strengths of all the experimental reinforced papers were greater than the 0.59 lb/in. peel strength of the commercial reinforced paper, Kaycel RSR-8525. Of the experimental papers, the ones containing 100-denier nylon had the highest peel strengths.

The wood-pulp paper containing 6 x 6 strands per inch of 100-denier nylon had the best physical properties of the papers that had been examined. Its dry breaking strength and abrasion resistance were as high as those of the 4-oz/yd^2 cotton fabric, for which physical properties are also given in Table I-21. The wet breaking strength and tearing strength of the paper were quite good; although, lower than those of the cotton fabric. The paper had poorer drape and hand and low air permeability.

(b) Latex-treated scrims

Although the reinforced papers previously prepared had reasonably good peel strengths, it was considered possible that better adhesion of the reinforcing yarns to the surface layers of the papers would result in better tensile properties. Reinforced papers were prepared from nylon scrim treated with various latexes and two 8 x 8 in. handsheets of bleached kraft wood pulp that weighed 1.4 g each. The handsheets were made from kraft pulp that had been beaten to a freeness of 760 Canadian standard. The nonwoven scrims contained 8 x 8 strands per inch of 100-denier nylon yarn. They were prepared on a 10 x 10-in. pin frame, and the latex adhesives were applied with a small paint brush. Care was exercised to apply the adhesives as uniformly as possible, but this was difficult. Immediately after the latex was applied, the scrim was placed between two handsheets, the sandwich was pressed, first with a roller, then between blotters for 5 minutes at 600 psi. Only one of the papers was heated during pressing—the sheets containing Gen-Tac-treated scrim were pressed for 5 minutes at 600 psi and 160°C. The formulas for the adhesives used in this study, the amounts of adhesive applied to the scrims, and the peel strengths of the reinforced papers are given in Table I-22.

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Table I-22. Peel Strengths of Wood-Pulp Papers Reinforced with Nylon Scrim Treated with Various Adhesives

Adhesive	Material	Parts by weight on product basis	Solids add-on, %	Peel strength, lb/in.
Vistanex	Vistanex L-120	100	10-12[a]	0.97
	Vistanex LM, Type MH	35		
	Piccolyte S-115-L	125		
	Skelly Solve "B"	1780		
Gen-Tac	Gen-Tac	90	10[a]	0.95
	Hylene MP	10		
	Cab-O-Sil	2		
Ubabond H-511	Ubabond H-511	50	9[b]	0.74
	2-Butanone	50		
Ubabond H-511	Ubabond H-511	70	13[b]	1.74
	2-Butanone	30		
Ubabond H-511	Ubabond H-511	90	22[b]	1.56
	2-Butanone	10		
Poly(vinyl pyrrolidone/vinyl acetate), I-535	Poly(vinyl pyrrolidone/vinyl acetate) I-535	20	12[b]	0.60
	Geon 427	20		
	2-Butanone	50		
	Toluene	50		
	Good-rite Plasticizer GP	3		
Rhoplex B-15[c]			25	negligible

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[a] Solids add-on was determined by extraction of the treated paper with 2-butanone.

[b] Solids add-on was determined by increase in weight of the paper.

[c] Rhoplex B-15 was applied as an aftertreatment, not to scrim.

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In one experiment, untreated scrim was sandwiched between two dry handsheets, and the sandwich was wet thoroughly with water. The wet sandwich was pressed between blotters for 1 to 2 minutes at 200 psi pressure, then dried for 10 to 15 minutes at 120°C. The reinforced papers were bonded by impregnation with Rhoplex B-15. The add-on of Rhoplex B-15 solids was 25%.

The peel strength of the Rhoplex-impregnated paper that contained untreated scrim was negligible. As shown in Table I-21, peel strengths ranging from 0.93 to 1.7 lb/in. were obtained when untreated scrim was sandwiched between waterleafs of wood pulp, rather than dry handsheets, and the reinforced papers were impregnated with latex.

It was very difficult to separate the layers of any of the papers by hand. At approximately equal levels of add-on of the adhesives studied, Ubabond H-511 gave papers with the highest peel strengths. Ubabond H-511 was evaluated at three levels of add-on and papers containing 13% of the adhesive solids had the highest peel strength, 1.74 lb/in.

(2) Nylon textryl-reinforced paper

In our previous work, we found that reinforcement of wood-pulp papers increased the dry and wet breaking strengths, tearing strengths, abrasion resistance, and crease recovery of the paper. However, the use of a scrim as a reinforcing material had several drawbacks: the snag resistance of scrim-reinforced papers was poor, the peel strength was not as great as desired, and permanent distortion could occur easily in the diagonal direction. Studies of other reinforcing materials have been undertaken in attempts to overcome these deficiencies.

An examination of a sample of a calendered nylon textryl revealed that it was very difficult to tear. Because of its high strength and elongation, the textryl would be expected to have good snag resistance and the textryl was not easily permanently distorted in the machine, cross, or diagonal directions. Although calendered textryls are similar to conventional papers in being dense, smooth, and stiff, and consequently are not suitable alone for our use, the textryls offered possibilities for reinforcing wood-pulp papers. It was postulated that the good physical properties of the nylon textryl could be utilized by sandwiching a textryl between sheets of wood-pulp paper and hot calendering to make them adhere.

Handsheets were prepared that contained a nylon textryl paper sandwiched between two sheets of wood pulp papers. The wood-pulp sheets and the nylon sheets were 8 x 8 in. and weighed 1.2 g each.

The wood-pulp handsheets were prepared from bleached kraft pulp, as described previously. The nylon textryls contained 30% of nylon fibrid 101 and 70% of 1.5-denier 0.25-in. nylon staple. A slurry of 60 g of fibrid 101 (20% solids) in 3.6 liters of water was prepared by first dispersing the fibrid, in several portions, in a Waring Blendor for 1 minute and then stirring the slurry at a moderate rate for 30 minutes with a propellor agitator. Then 45 g of nylon fiber dispersed in 8.4 liters of water was added. Stirring was continued for 1 hour after the two slurries were mixed. The nylon fiber slurry was made by dispersing 45 g of the fiber in 8.4 liters of water containing 0.016% by weight of Santomerse SX. This dispersion was stirred for 30 minutes prior to adding it to the fibrid slurry. The slurry mixture was used to prepare 10 to 15 replicate handsheets. Waterleafs were formed in a Williamson 8 x 8 in. sheet mold with a 100-mesh stainless steel screen. The waterleafs were removed from the screen on a blotter, pressed between blotters for 1 to 2 minutes at 200 psi pressure, and then dried on an electric dryer for 10 to 15 minutes at 120°C. The dried handsheets weighed 1.2 g each.

The reinforced paper was made by sandwiching a nylon textryl handsheet between two 1.2-g wood-pulp handsheets. The sandwich was placed between two metal sheets and laminated in a hydraulic press. The nylon textryl did not fuse and bond the wood-pulp surface sheetings as well as was expected. The conditions required to obtain even moderate bonding scorched the wood-pulp sheets. The breaking and tearing strengths of the paper were low compared to papers reinforced with nylon scrim. Also the paper was very stiff, and the adhesion between the wood-pulp sheets and the textryl sheet was poor.

b. Nylon-wood pulp papers

The studies of nonreinforced papers indicated that papers containing 50% kraft wood pulp and 50% nylon fibers were the most promising of the numerous types evaluated for the overgarment although they were deficient in many properties. The studies described in the immediately preceding section showed that reinforcement of papers with scrims offered a means of overcoming or minimizing many of these deficiencies. Therefore additional studies were made to develop the best type of reinforcing material for and the best method for producing reinforced nylon-wood pulp papers.

The procedures used for preparing the 50% nylon-50% wood pulp waterleafs and papers for these studies are described in Section III-C-1-e.

(1) Scrim-reinforced papers

Scrims made of nylon yarn were the most effective of the various types tried for reinforcing papers for use in the protective overgarment. Various other types of scrims were investigated but were not as promising

(a) Nylon scrims

Nylon scrims were shown to be effective for reinforcing wood-pulp papers in Section III-C-2-(1) and a scrim with 6 x 6 strands per inch of 100-denier nylon yarn appeared to be desirable. Ubabond H-511 was the most effective of several adhesives that were tried for bonding the scrim to the surface layers of the papers, but it caused spotting of the surfaces of the papers.

Further trials of scrims of different constructions and of other adhesives were made with 50:50 nylon-wood pulp papers.

(aa) Adhesives

Seven adhesives were compared for bonding a nonwoven scrim with 6 x 6 strands per inch of 100-denier nylon yarn to dry handsheets of 50:50 nylon-wood pulp handsheets. The adhesives were applied to the scrim by spraying, and the scrim was immediately placed between two handsheets. The combination sheet was pressed together with a roller and evaluated for peel strength after drying and conditioning. The adhesive used and the peel strengths of the reinforced papers so prepared are listed in Table I-23.

Table I-23. Formulations of Adhesives.

Product	Formula[a]	Solids applied, approx. %[b]	Peel strength, lb/in.
Formica Contact Cement	70% Formica Contact Cement 30% 2-Butanone	15	c
Splic-It	100% Splic-It	10 5	d 1.4
Vultex 1-S-1052	20% Vultex 1-S-1052 80% water	10	<0.1
Vultex 1-S-1009	20% Vultex 1-S-1009 80% water	10	<0.1
ARCCO SC-377	100% ARCCO SC-377	10	1.2
U. S. Royal Industrial Adhesive M 6256	100% U. S. Royal Industrial Adhesive M 6256	10	c
PR-153	70% PR-153 25% water 5% ethyl alcohol	10	c

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[a] Parts by weight on product basis.

[b] Based on total weight of paper.

[c] Very poor or no adhesion.

[d] Could not separate scrim from paper.

The papers containing scrim treated with 5% of either Splic-It or ARCCO SC-377 had higher peel strengths than the papers containing scrim treated with the other adhesives. Papers containing 10% solids add-on of Splic-It had the highest peel strength; the layers of this paper could not be separated by hand as compared to a peel strength of 1.7 lb/in. for paper containing 13% Ubabond H-511. Splic-It did not appear to affect the flexibility of the papers appreciably, and it did not cause color spotting of the paper. Splic-It was easily applied to the yarns and adhered very well.

Our previous studies of the effects of the structure of scrim on the properties of reinforced wood-pulp paper showed that paper containing 6 x 6 strands per inch of 100-denier nylon was the best of those studied. A 50% nylon and 50% wood pulp paper reinforced with 9 x 9 strands per inch of 70-denier nylon yarn was prepared in the hope that the use of the lower denier yarns would increase the abrasion resistance of the paper by giving a paper with a smoother surface. Also, it was hoped that the increased number of yarns would give more points of adhesion and thus increase the adhesion between the yarn and the surface layers. For control purposes, a nylon-wood pulp paper reinforced with 6 x 6 strands per inch of 100-denier nylon was prepared and evaluated.

These papers were made by placing the nonwoven scrim (without adhesive) between two 50:50 nylon-wood pulp water leafs and pressing them between blotters for 2 minutes at 200 psi. Then they were dried 10-15 minutes at 120°C. The papers were bonded by impregnating them to apply 25% Rhoplex B-15 solids and drying 30 minutes at 120°C. Data on the properties of papers containing scrims of the two constructions are given in Table I-24.

The tearing strength of the paper containing 9 x 9 strands per inch of nylon yarn was slightly greater than the tearing strength of the paper containing 6 x 6 strands per inch of 100-denier nylon yarn. However, the latter had greater peel strength, abrasion resistance, and air permeability than the paper that contained 9 x 9 strands per inch of 70-denier nylon. Increasing the number of yarns per inch also increased the stiffness of the paper. It was concluded that 6 x 6 strands per inch of 100-denier nylon yarn was the best construction for the reinforcing scrim.

Table I-24. Properties of Scrim Reinforced Nylon-Wood Pulp Papers

	50% nylon-50% wood pulp paper reinforced with 6 x 6 strands of 100 denier nylon yarn	50% nylon-50% wood pulp paper reinforced with 9 x 9 strands of 70 denier nylon
Total weight, oz/yd^2	2.7	2.8
Thickness, mils	12.0	13.5
Breaking strength, lb/in.	30.3	29.1
Elongation at break, %	20.3	15.0
Elmendorf tear, g	1203	1357
Abrasion resistance, weight loss after 200 cycles, %	4.7	5.9
Air permeability, $ft^3/min/ft^2$, 0.5 in. water	21	12
Stiffness, mg	86.6	164.3
Peel strength, lb/in.	0.47	0.27

(bb) Comparison of experimental nylon scrim-reinforced nylon-wood-pulp paper with commercial papers

At the time this comparison was made, Ubabond H-511 was the bes of the adhesives that had been evaluated for bonding the nylon scrim in the papers. The papers that were compared and their properties are listed in Table I-25. The reinforced nylon-wood pulp paper was made with a 6 x 6 nonwoven scrim of 100-denier nylon yarn. The yarn contained 1.5-denier, 0.25-in. nylon staple. Prior to use, the scrim was sprayed with a solution of 50 parts (by weight) of Ubabond H-511 in 50 parts of 2-butanone. Then it was placed between two nylon-wood pulp handsheets and compressed in a hydraulic press for 2 minutes at 400 psi. The amount of Ubabond H-511 solids applied to the scrim was 10-12% of the total weight of the final sheet. The paper was impregnated to apply 25% of Rhoplex B-15 solids and dried at 120°C for 30 minutes. To impart liquid repellent properties, the paper was next padded with a bath containing 2% of FC-208 solids and 0.25 Phobotex FTC solids to apply 100% wet pickup. Finally the sheet was dried 6 minutes at 150°C.

Kaycel 100 is a commercial wood-pulp paper also reinforced with 6 x 6 strands per inch of 100-denier nylon but it is not bonded. For comparison with the reinforced nylon-wood pulp paper, Kaycel 100 was treated to apply Rhoplex B-15, FC-208, and Phobotex FTC as described above.

The nylon-wood pulp paper had higher wet and dry breaking strengths, resistance to wet and dry abrasion, air permeability, crease recovery, bursting strength, and puncture strength. The treated Kaycel paper had higher tearing strength and the best drape. The handle of both papers was good. Compared to Kaycel RSR-8514 and Kaycel RSR-8525, the two best commercial papers that we have found, the nylon-wood pulp paper had the highest breaking strength, bursting strength, puncture strength, and abrasion resistance. Kaycel RSR-8525 had the best handle and drape and the highest tearing strength.

Table I-25. Properties of Scrim-Reinforced Nylon-Wood Pulp Paper and Knycel Papers

	50% nylon-50% wood pulp paper reinforced with 6 x 6 strands of 100 denier nylon yarn[a]	Knycel 100 cellulose wadding reinforced with 6 x 6 strands of 100 denier nylon[a]	Kaycel RSR-8514 cellulose wadding reinforced with 100 denier nylon[b]	Knycel RSR-8525 cellulose wadding reinforced with 100 denier nylon in warp and 210 denier in filling[b]
Total weight, oz/yd^2	3.0	3.4	2.5	3.0
Thickness, mils	14.7	10.1	9.6	10.5
Breaking strength, lb/in.				
Dry	34.3			
Machine		22.4	20.5	24.0
Cross		19.4	11.2	21.2
Wet	28.3			
Machine		15.2	11.6	16.0
Cross		16.1	9.0	19.2
Elongation at break, %				
Dry	16.3			
Machine		27.4	7.5	2.5
Cross		21.6	4.5	2.4
Wet	25.0			
Machine		21.2	6.2	1.8
Cross		21.2	6.6	2.6
Elmendorf tear, g	1043			
Machine		1676	2195	2266
Cross		986	1840	
Abrasion resistance,				
Dry				
Cycles	200	200	200	200
Weight loss, %	3.4	8.4	11.9	1.48
Wet				
Cycles to rupture	448	209	37	41
Air permeability, ft^3/min/ft^2, 0.5 in. water	29	13	16	10
Crease recovery, %	55	41	43	46
Stiffness, mg	84	22	22	47
Bursting strength, psi	81	62	70	80
Puncture strength, lb	5.7	2.6	1.9	2.3
Drape	fair	good	fair	good
Handle	good	good	harsh	soft

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[a] Treated to apply 25% Rhoplex B-15, 2% FC-208, and 0.25% Phobotex FTC solids on weight of paper.

[b] Made by Kimberly-Clark Corporation; has abrasion [illegible]

(b) Other scrims

Cotton, rayon, polyethylene, and vinylidene chloride yarn scrims were also tried as reinforcements for 50:50 nylon-wood pulp papers. As mentioned previously, none of these was found to be as desirable as nylon scrims. The nylon-wood pulp waterleafs used in these trials weighed 1.1 oz/yd^2. One 8 x 8 inch waterleaf was placed on each side of a scrim and the layers were pressed together between blotters in a hydraulic press at 200 psi. Then the papers were dried 10 to 15 minutes at 120°C. Finally they were impregnated with Rhoplex B-15 and again dried.

Descriptions of the scrims used and the properties of the papers produced are given in Table I-26.

(2) Nylon textryl-reinforced paper

A paper was made from two 0.85 oz/yd^2 nylon-wood pulp sheets and one 0.85 oz/yd^3 nylon textryl sheet to determine primarily if such a paper would have better puncture resistance than papers with other reinforcing materials. The wood-pulp sheets were made by the usual procedure. The nylon textryl sheets contained 70% of 1.5-denier, 0.25-in. nylon staple and 30% of nylon fibrid 101 and were made by the procedure described in Section III-C-1-j. The paper was treated to apply 25% Rhoplex B-15 solids.

The properties of this paper are given in Table I-27 along with those of a nylon scrim-reinforced paper.

The puncture strength of the nylon textryl-reinforced paper was excellent compared to the puncture strength of similar paper reinforced with scrim, but the paper was too stiff and had too poor draping qualities to be of interest for the overgarment.

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Table I-28. Properties of Reinforced Nylon-Wood Pulp Papers

Scrim			Thickness, mils	Weight, oz/yd^2	Breaking strength, lb/in.		Elongation, at break, %	Elmendorf tear, g	Abrasion resistance, % wt loss after 200 cycles	Air permeability, ft^3/min/ft^2, 0.5 in. water	Stiffness, mg	Bursting strength, psi
Yarn	Count	Weight, oz/yd^2			Dry	Wet						
No reinforcement[a]			8.2	3.5	22.5	9.0	-	694	1.35	32.1	-	-
Cotton[b]	6 x 6	2.2	28.3	5.1	43.0	25.4	-	d	1.76	34.0	-	-
Rayon[c]	4 x 4	1.0	19.4	4.1	29.2	10.0	-	1401	5.32	30.1	-	-
170-Denier Polyethylene	6 x 6	-	12.5	3.9	31.5	-	26.6	2312	-	14.5	160	152
400-Denier Rovana	6 x 6	-	14.1	3.9	38.8	-	25.0	2504	2.8	37.5	133	84
100-Denier nylon	6 x 6	-	14.7	3.0	34.3	-	16.3	1043	3.4	29.0	84	81

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[a] The nonreinforced paper contained 30% Rhoplex B-15 solids; the others contained 25% Rhoplex B-15 solids.

[b] Dixienet 55[illegible]-40047 from Swift Manufacturing Company.

[c] Style BR-[illegible] from Wellington Sears. It is loom-bonded with neoprene.

[d] Scrim pulled out of paper; consequently, tearing strengths could not be measured accurately.

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Table I-27. Physical Properties of Nylon Textryl-Reinforced Paper

	50% nylon-50% wood pulp reinforced with nylon textryl[a]	50% nylon-50% wood pulp paper, reinforced with 6 x 6 strands of 100 denier nylon yarn[b]
Weight, oz/yd^2	3.4	3.0
Thickness, mils	8.4	14.7
Breaking strength, lb/in.		
Dry	34.3	29.5
Wet	28.3	
Elongation at break, %		
Dry	16.3	
Wet	25.0	21.3
Elmendorf tear, g	611	1043
Abrasion resistance		
Dry		
Cycles	200	200
Weight loss, %	4.8	3.4
Wet		
Cycles to rupture	-	448
Air permeability, ft^3/min/ft^2, 0.5 in. water	16	29
Crease recovery, %	-	55
Stiffness, mg	175	84
Bursting strength, psi	-	81
Puncture strength, lb	9.5	5.7
Drape	poor	fair
Handle	poor	good

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[a] Paper contains 25% Rhoplex B-15 solids on weight of paper.

[b] Treated to apply 25% Rhoplex B-15, 2% FC-208, and 0.25% Phobotex FTC solids on weight of paper.

(3) Nonwoven fabric-reinforced papers

Nonwoven fabrics made from all nylon, all cellulose acetate, all viscose, and a 50:50 mixture of cellulose acetate and viscose fibers were evaluated as reinforcing materials for nylon-wood pulp papers.

The all cellulose acetate nonwoven fabric was made in the laboratory by hand carding 3.0-denier, 2.0-in. cellulose acetate fibers and cross laying made in the laboratory. The nylon fabric was made by hand carding 1.5-denier, 1.5-in. nylon fibers and cross-laying three layers of the carded fibers to form a fabric that weighed about 1.1 oz/yd^2. About 2% of Rhoplex B-15 solids was applied by spraying to bond the fabric. This fabric was combined with two 1.1 oz/yd^2 50:50 nylon-wood pulp sheets, prepared by the usual procedure, and the composite was bonded with 25% of Rhoplex B-15 solids.

Data on the properties of the cellulose acetate reinforced paper are given in Table 1-28. For comparison, data for a nylon-scrim-reinforced paper are also given in the table. The tearing strength of the nonwoven-reinforced paper was almost equal to the tearing strength of papers reinforced with nylon scrim. With the scrim-reinforced paper, a tear was started easily relative to woven fabrics but the tear was not easily propagated. The paper reinforced with nonwoven cellulose acetate fabric resisted the propagation of a tear nearly as well as the scrim-reinforced paper, but the nonwoven-reinforced paper seemed to resist initial tearing better than the scrim-reinforced paper. The scrim-reinforced paper had slightly better abrasion resistance and breaking strength than the paper reinforced with the cellulose acetate.

Attempts were made to prepare a nylon-wood pulp paper reinforced with a nonwoven nylon fabric made in this laboratory from 1.5 denier, 1.5-inch nylon fibers, but a strong uniform bond could not be obtained between the surface sheets and the nonwoven fabric.

One nonwoven fabric made from 100% viscose rayon and another made from 50% viscose rayon and 50% cellulose acetate were made by the Chicopee Manufacturing Company especially for this study. Each fabric weighed 1.0 oz/yd^2 and contained a Rhoplex binder. Papers were made with one layer of each of the nonwoven fabrics between two nylon-wood pulp sheets. They were treated to apply 25% Rhoplex B-15 solids. The final weight of each paper was 3.9 oz/yd^2.

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Table 1-28. Properties of Nylon-Wood Pulp Papers Reinforced with Nonwoven Fabrics [a]

Nonwoven fabric	Weight, oz/yd²	Thickness, mils	Breaking strength, lb/in.		Elongation, at break, %		Elmendorf tear, g		Abrasion resistance, % weight loss after 200 cycles	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg	Bursting strength, psi	Puncture strength, lb
			Machine	Cross	Machine	Cross	Machine	Cross					
100% Cellulose acetate	3.8	17.8	21.6		13.0		1164		5.9	20	236	-	-
100% Viscose	3.9	15.6	35.6	24.3	15.1	13.4	1230	1163	5.6	33	258	-	7.3
60% Viscose 50% Cellulose acetate	3.9	17.6	36.9	34.4	14.9	14.9	781	626	2.3	26	205	102	11.3
6 x 6 Nylon scrim reinforced	3.0	14.7	34.3		16.3		1043		3.4	29	84	81	5.7

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[a] Papers contained 25% Rhoplex B-15 solids on fiber weight.

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The tearing strength of the viscose nonwoven-reinforced paper was slightly greater than the tearing strength of the similar paper reinforced with nylon scrim. However, this nonwoven-reinforced paper resisted initial tearing better than the scrim-reinforced paper. The breaking strength of the paper in the machine direction of the nonwoven reinforcement was about the same as the breaking strength of the scrim-reinforced paper. The breaking strength of the paper in the machine direction of the nonwoven reinforcement was about the same as the breaking strength of the scrim-reinforced paper; the breaking strength of the paper in the cross direction of the nonwoven reinforcement was, as expected, slightly less. The scrim-reinforced paper had better abrasion resistance, puncture strength, and flexibility than the nonwoven-reinforced paper, but the nonwoven-reinforced paper had a softer hand than the scrim-reinforced paper. The drape of the paper was poor.

The breaking strength of the nylon-wood pulp paper reinforced with the viscose/acetate nonwoven fabric was about the same as the breaking strength of the nylon-wood pulp paper reinforced with the nonwoven all-viscose fabric. The puncture strength, flexibility, and abrasion resistance were higher for the paper reinforced with the viscose/cellulose acetate fabric, but the tearing strength was lower.

(4) Woven fabric-reinforced papers

Woven nylon fabrics are available in very light weights, and the use of a fabric of this type as a reinforcement for nylon-wood pulp paper was investigated as a possible means of producing a light-weight material for the protective overgarment that would have high tear strength. As expected, the major problem in making a reinforced paper of this type was obtaining satisfactory adhesion between the nylon fabric and the nylon-wood pulp surface sheets without adversely affecting other properties.

A 1.1 oz/yd^2 rip-stop nylon fabric obtained from Frank Ix and Sons was used in all of the trials of this series. The surface sheets were made from 50% nylon-50% bleach kraft pulp by the usual procedure and weighed 1.1 oz/yd^2. The adhesives that were tried were EC-1729, Kymene, Uformite MM-46, Geon 576, and a combination of Rhoplex B-15 and Rhonite 401.

In trials with EC-1729, the nylon-wood pulp sheets were treated to apply 25% Rhoplex B-15 solids and, after drying, they were sprayed to apply about 50% solids of EC-1729. A piece of 1.1 oz/yd^2 nylon fabric was placed over the adhesive-treated paper, and the combination was placed between two Teflon sheets and pressed by passing it between the rollers of a laboratory padder. After air drying, the average weight of the laminate was 3.5 oz/yd^2.

As shown in Table I-29, the laminate had higher breaking strength (wet and dry), puncture strength, bursting strength, and tearing strength, than the nylon-wood pulp paper. The laminated material had good dry and wet abrasion resistance. With the nylon fabric in contact with the abradant an average of 225 cycles was required to rupture the dry nylon layer, but 760 cycles was required to wear a hole through the entire laminate.

The laminate weighed slightly more than planned because of the difficulty encountered in controlling the amount of adhesive applied between the paper and the fabric. The peel strength of the laminated material was poor.

Several methods were tried for making laminates with Rhoplex B-15 combined with Rhonite 401 as the adhesive. The first method was as follows: A paper handsheet and a piece of nylon fabric were placed between two copper screens to hold them together and dipped in a bath containing 89% of Rhoplex B-15 latex, 10% of Rhonite 401, and 1% of concentrated ammonium hydroxide. The impregnated material, while still held between the copper screens, was passed through a padder to remove excess liquids. The screens were removed and the laminate was heated 5 minutes at 150°C. The adhesive add-on was varied by changing the pressure of the padder rolls to obtain different wet pickups. Samples were prepared with 25, 30, 40, and 50% solids add-on of adhesive.

The peel strengths of these samples were 0.75, 1.20, 1.25, and 1.35 lb/in., respectively. These values are high compared to those for most of the scrim-reinforced nylon-wood pulp papers, but they are conside ably lower than the strength of the paper, which is about 3.4 lb/in. The peel strengths of laminates containing 30% or more solids add-on were considered border-line, but acceptable, for use of the laminates in the protective overgarment. The laminates so produced were stiffer than the scrim reinforced nylon-wood pulp paper treated with Rhoplex B-15.

Table I-29. Properties of a Nylon Fabric-Paper Laminate and Reinforced Nylon-Wood Pulp Paper

	Laminate of nylon fabric and nylon-wood pulp paper	50% nylon-50% wood pulp paper reinforced with 6 x 6 strands of 100 denier nylon yarn[a]
Total weight, oz/yd^2	3.5	3.0
Breaking strength, lb/in.		
Dry		34.0
Machine	43.0	
Cross	46.0	
Wet		28.3
Machine	41.0	
Cross	34.0	
Elongation at break, %		
Dry	-	16.3
Wet	-	25.0
Elmendorf tear, g		1043
Machine	1709	
Cross	1456	
Abrasion resistance, cycles to rupture surface layer,		
Dry	225	200[b]
Wet	1088	457
Air permeability, ft^3/min/ft^2, 0.5 in. water	14	29
Stiffness, mg		84
Machine	84	
Cross	102	
Bursting strength, psi	>120	81
Puncture strength, lb	14.7	5.7

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[a] Treated to apply 25% Rhoplex B-15, 2% FC-208, and 0.25% Phobotex FTC on weight of paper.

[b] Did not rupture; 3.4% weight loss after 200 cycles.

[illegible]

Attempts were made to make laminates with the B-15-Rhonite 401 applied to the nylon-wood pulp sheets and to the nylon fabric by brushing or by knife coating. However, when the adhesive was applied by these methods, either to the paper or to the fabric, attempted lamination failed.

Attempts to make laminates of the nylon fabric and nylon-wood pulp sheets with Kymene as the adhesive were unsuccessful. The Kymene was applied by brushing (1) to the paper only, (2) to the fabric only, and (3) to both paper and fabric. No bonding was achieved after pressing the laminates 5 to 8 minutes at 150°C.

Nylon-wood pulp sheets and nylon fabric treated with Uformite MM-46 in the same manner as with Kymene also did not produce satisfactorily bonded laminates. The use of 1% of Catalyst A, 1% of glacial acetic acid, or 1% of benzenesulfonic acid with the resin did not improve the bonding.

Geon 576 latex (56.8% solids) was also tried as an adhesive. It was brushed on nylon-wood pulp paper to thoroughly wet them and a laminate of treated sheets and nylon fabric was cured in a press for 5 minutes at 150°C. The laminate formed was well bonded, but it was boardy (the fabric and paper were practically embedded in a Geon 576 film). Another laminate made in the same manner with latex containing 28.4% solids was not satisfactorily bonded. Acceptable bonding was obtained with latex containing approximately 38% solids, but the laminate was still boardy.

In an attempt to reduce the penetration of the adhesive into the paper, the Geon 576 was thickened with carboxymethylcellulose (CMC). The composition used contained 37.8% of Geon 576 solids and 2.7% of CMC. It was applied to the paper handsheet by brushing, and a laminate was made as described above. A slight but insufficient improvement was obtained in the hand of the laminate.

Nylon-wood pulp sheets were prepared to contain: (1) 50% wood pulp, 40% of 1.5 denier, 0.25-in. nylon, and 10% of Fibrid 101, and (2) 50% of wood pulp, 40% of nylon, and 10% of Fibrid 201. The sheets were dried 10 minutes at 135°C. Laminates of each sheet and nylon fabric cured in a press for 5 to 8 minutes at 150°C were not bonded satisfactorily.

c. Dacron papers

Two types of Dacron papers were investigated for possible use in the protective overgarment. One was a Dacron textryl paper reinforced with Dacron scrim; the other was a Dacron D-90-wood pulp paper reinforced with nylon scrim. The former had low tearing strength and low abrasion resistance and showed no qualities to make it of interest; the latter had particularly good hand and drape, but some physical properties were not as satisfactory as those of comparable nylon-wood pulp papers.

(1) Dacron textryl paper

Dacron textryl handsheets containing 80% of 1.5-denier, 0.25-in. staple Dacron fiber and 20% of Dacron fibrid 201 were prepared as described in Section III-C-1-j. Nonwoven scrim containing 6 x 6 strands per inch of 100-denier Dacron yarn was placed between two of the handsheets and the sandwich was pressed between aluminum sheets for 5 minutes at 205°C. The final weight of the paper was 2.7 oz/yd^2.

The properties of the Dacron-reinforced Dacron textryl paper are given in Table I-30. The properties of a nylon-reinforced nylon-wood pulp paper are also given in the table for comparison.

The breaking strength of the Dacron paper was almost equal to the breaking strength of the nylon-wood pulp paper reinforced with nylon scrim. However, the treating strength of the reinforced Dacron textryl paper was relatively low, and the weight loss of the paper due to abrasion was high (9.3%) compared to the reinforced nylon-wood pulp paper. Due to the low tearing strength and abrasion resistance of the reinforced Dacron textryl papers they were not of further interest.

Table I-30. Properties of Reinforced Dacron Papers

	Dacron textryl reinforced with 6 x 6 strands of 100 denier Dacron	75% Dacron D-90 25% wood pulp paper reinforced with 6 x 6 strands of 100 denier nylon yarn[a]	63% Dacron D-90 14% nylon 23% wood pulp reinforced with 6 x 6 strands of 100 denier nylon yarn[a]	50% nylon 50% wood pulp reinforced with 6 x 6 strands 100 denier nylon yarn[b]
Total weight, oz/yd²	2.7	2.9	3.1	3.0
Breaking strength, lb/in.[c]	32.8	17	15	34
Elongation at break, %[c]	16	31	27	16
Elmendorf tear, g	640	1811	1901	1043
Abrasion resistance,				
Cycles	200	176	200	200
Weight loss, %	9.3	ruptured	ruptured	3.4
Air permeability, ft³/min/ft², 0.5 in. water	77	210	165	29
Stiffness, mg	98	78	38	84
Bursting strength, psi	-	58	63	81
Handle	poor	excellent, soft	excellent, soft	good
Drape	poor	excellent	excellent	poor

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[a] Treated to add 25% Rhoplex B-15 solids.

[b] Data repeated from Table I-27.

[c] Values for Dacron papers were determined on an Instron tester; values for nylon paper, on a Scott IP-4 tester.

(2) Dacron-wood pulp papers

Nylon-scrim reinforced papers were made with handsheets containing 75% of Dacron D-90 and 25% of wood pulp and with handsheets containing 63% of Dacron D-90, 14% of nylon, and 23% of wood pulp. The handsheets weighed about 1.3 g (8 x 8 in.). The scrim used contained 6 x 6 strands per inch of 100-denier nylon yarn and they were sprayed with Splic-It. Immediately after application of the adhesive, the scrim was placed between two handsheets, and the sandwich was pressed 5 minutes at 600 psi. The papers were treated to apply 25% Rhoplex B-15 solids and dried 30 minutes at 120°C.

The properties of these papers are also given in Table I-30.

The 75:25 Dacron-wood pulp paper that was reinforced with 6 x 6 strands per inch of 100 denier nylon had better tensile properties than the nonreinforced 75:25 Dacron-wood pulp paper (Table I-19). However, the reinforcement did not improve the tensile properties as much as expected. The abrasion resistance, flexibility, hand, and drape of the reinforced paper was about the same as those of the nonreinforced paper.

The reinforced 63:14:23 Dacron-nylon-wood pulp paper had increased abrasion resistance and bursting strength, decreased breaking strength, and improved flexibility, compared to the reinforced 75:25 Dacron-wood pulp paper. The tearing strength, hand, and drape of the two papers were about the same. Compared to the nylon-wood pulp paper, the paper containing Dacron D-90, nylon, and wood pulp had much better hand, drape, and flexibility, and better tearing strength. The abrasion resistance was somewhat lower than that of the nylon-wood pulp paper. The nylon-wood pulp paper had a higher bursting strength and a much higher breaking strength.

Except for breaking strength and possibly cost, the reinforced paper containing Dacron D-90, nylon, and wood pulp appears to be suitable as a base material for the protective overgarment.

Values for D ron papers were determined on an Instron test · values for nylon paper, on a Scott IP-4 tester.

D. Treatments for Papers

The work on papers for the protective overgarment that has been described in the preceding sections (Sections III-A, B, and C) was directed mainly to the development of a paper that would have the basic properties, such as tensile strength and tear resistance, required for satisfactory durability. Other qualities were necessary in materials for the overgarment that it appeared could best be imparted by aftertreatment of the papers.

Resistance to liquid CW agents was of prime importance; resistance to burning and to water, and maximum flexibility and softness were highly desirable qualities. Studies of means of obtaining these qualities were carried on concurrently with the development of the papers and attempts were made to obtain more than one of the effects simultaneously.

The problem of finding a finishing treatment to make the Rhoplex B-15-bonded nylon-wood pulp paper resistant to oil, water, and flame simultaneously was complicated by the presence of the several different types of materials in the paper. Most of the conventional and better known flame retardants for cellulose were not effective when the acrylic resin was present, and some flame retardants that were found to be effective on Rhoplex B-15-bonded cellulose paper were not effective when nylon was present in the paper. Although we were not restricted to the use of an acrylic resin for bonding the paper, this type of resin was found to be most effective of those tried for improving the physical properties of the paper. Finding a satisfactory means of providing flame-retardant properties was further complicated by the requirement that the treatment used should not impair the resistance to liquid CW agents that was provided by the treatments with FC-208 and that it should not produce an undesirable handle.

1. Softeners and plasticizers

A major drawback to the use of paper as a garment material, that was recognized at the start of the program, was the self-describing characteristic of paperiness. In textile terminology, papers generally have poor hand, flexibility, and drape. The all-wood pulp papers that were examined in the early stages of our program were unsatisfactory in these characteristics and the use of softeners and plasticizers was investigated for improving these qualities as described below. The nylon-wood pulp papers that were developed in the program were much better than the all-wood pulp papers in these qualities and aftertreatments to improve them were of less importance.

The studies of the effects of softeners and plasticizers were made on handsheets weighing about 3.5 g per 8 x 8 inch sheet made from semi-bleached kraft pulp beaten to a freeness of 600 Canadian standard as described in Section III-C-1. The handsheets were held between two 60-mesh wire screens during wet aftertreatments. A handsheet was dipped in a bath of Rhoplex B-15 and then pressed in a hydraulic press to give a 25% solids add-on. The screens were then removed and the sheets were dried 30 minutes at 120°C. The Rhoplex B-15 treated papers were then treated to apply 3% of a softener or 10% of a plasticizer. The softeners that were investigated were Epolene E, a polyethylene emulsion; Syl-Soft 12, a silicone softener; C_{20} "oxo" alcohol; and Aliquat 336 (tricapryl monoethyl ammonium chloride). The plasticizers investigated were urea, triethylene glycol, and Carbitol (diethylene glycol monoethyl ether). The properties of the papers containing the softener or plasticizer are given in Table I-31, along with the properties of wood-pulp paper containing no softener or plasticizer.

The softeners were more efficient than the plasticizers for reducing the stiffness of the paper. Syl-Soft 12 and Aliquat 336 gave the paper the best handle, drape, and flexibility, but both drastically reduced the breaking strength.

Table I-31. Properties of Wood Pulp Papers[a] Containing Softeners or Plasticizers

Softener or plasticizer	Add-on, %	Breaking strength, lb/in.	Elmendorf tear, g	Stiffness, mg	Drape	Handle
None	-	37	164	222	poor	harsh, boardy
Triethylene glycol	10.0	43	180	100	poor	boardy
Carbitol	10.0	23	177	211	poor	boardy
Urea	10.0	28	155	111	fair	soft
Aliquat 336	3.0[b]	10		111	fair	soft
C_{20} "Oxo" alcohol	3.0	12	126	89	poor	tacky
Epolene E	3.0[c]	14	138	133	poor	harsh, boardy
Xyl-Soft 12	3.0[c]	3	38	22	good	very soft

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[a] Each handsheet contained 25% solids add-on of Rhoplex B-15.

[b] Approximately 1% solids.

[c] Add-on of solids, %.

Therefore, wood-pulp papers containing no Rhoplex B-15 were prepared and treated to apply 3%, 1%, 0.5%, and 0.05% of Syl-Soft 12 or Aliquat 336 to determine the optimum concentration of each softener to give the paper the best over-all properties. The properties of the softened papers along with the properties of a similar paper containing no softener are given in Table I-32.

All levels of add-on of softener studied increased the handle and drape of the wood-pulp paper and decreased the stiffness, tearing strength, and breaking strength of the paper. Because of the adverse effect of the softener on the strength, it was concluded that the softener add-on should be less than 0.5%.

Papers were impregnated with mixtures of Aliquat 336 or Syl-Soft 12 and Rhoplex B-15 to determine the effect of the softener on the paper when applied with the latex.

Properties of wood-pulp papers containing 0.1% softener and 25% Rhoplex B-15 are given in Table I-33. The properties of wood-pulp paper containing 25% Rhoplex B-15 but no softener are given for comparison.

Syl-Soft 12 did not improve the handle, drape, or flexibility of the latex-impregnated paper; it decreased the tearing strength and elongation and increased the breaking strength of the paper. The breaking strength value of the paper treated with Syl-Soft 12 was unexpected and is probably higher than the true value of the paper. Aliquat 336 improved the handle and decreased the stiffness of the latex-impregnated paper without seriously lowering the tearing and breaking strengths of the paper. Aliquat had no noticeable effect on the drape of the paper.

Table I-32. Properties of Wood-Pulp Paper[a] Containing Softeners

	Add-on, %	Breaking strength, lb/in.	Elmendorf tear, g	Stiffness, mg	Drape	Handle
Syl-Soft 12	3.0	2.9	34	55	good	good
	1.0	5.0	54	48	fair	good
	0.5	7.8	104	79	fair	fair
	0.05	10.5	112	133	poor	fair
Aliquat 336	3.0	5.4	50	33	fair	good
	1.0	5.4	82	135	fair	good
	0.5	6.5	66	159	poor	fair
	0.05	6.8	120	177	poor	fair
Control	-	18.7	125	335	poor	poor

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[a] 8 x 8-in. handsheets prepared from semi-bleached kraft pulp, weighing 3.5 g before softener was applied.

Table I-33. Properties of Wood-Pulp Papers Impregnated with Mixtures of Rhoplex B-15 and Softener[a]

Softener	Add-on, %	Breaking strength, lb/in.	Elongation at break, %	Elmendorf tear, g	Stiffness, mg	Drape	Handle
Syl-Soft 12	0.1	40.8	8.8	138	186	poor	poor
Aliquat 336	0.1	29.3	5.0	163	102	poor	fair
None		33.4	10.0	176	153	poor	poor

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[a] Each handsheet contained 25% solids add-on of Rhoplex B-15.

2. Resistance to liquid CW agents and water

Resistance to penetration by liquid CW agents was a prime requirement in the material for the protective overgarment and the investigation of methods of imparting this property to papers was started early in the program. Resistance to water was considered to be a desirable, but not an essential property.

a. Screening of commercial materials for oil and water repellency

The following methods were used for the initial screening of materials for resistance to penetration by the liquid CW simulant, bis(2-ethylhexyl)hydrogen phosphite, and by water: (1) determination of the contact angle between the liquid and the material, (2) determination of the time required for the liquid to be absorbed by the material, and (3) determination of the time required for the liquid to penetrate the thickness of the material. These methods are described in detail in Section A of the Appendix. These materials were also examined for water resistance. The materials evaluated and the results are given in Table I-34. Contact angles were measured but are not given in the tables since they did not show any relationship to absorption or penetration time. Comparable data on some nonwoven fabrics, woven fabrics, films, and foams are also included in this table. Descriptions of the materials are given in Section B of the Appendix. The conclusions from the evaluation are summarized here.

The CW simulant rapidly penetrated all the papers except the laminated papers. Water penetrated all of the uncoated papers except the creped paper, Kaycel 101-3, and Kaycel RSR-8525. The coated (or laminated) papers were resistant to penetration by water or CW simulant, but these papers are not suitable for clothing because of their low permeability to water vapor and to air.

Both water and the CW simulant rapidly penetrated all the woven and nonwoven fabrics tested, except the poplin fabric. This fabric was not penetrated by water, but it took only 120 seconds for penetration by the CW simulant.

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Table I-34. Resistance of Commercial Materials to Liquid CW Simulant and to Water

	Water		CW simulant	
	Absorption time, sec.	Penetration time, sec.	Absorption time, sec.	Penetration time, sec.
PAPERS[a]				
A. Miscellaneous Papers				
Flexrope 8235	instantly	instantly	instantly	1
Flexrope 8345	instantly	instantly	instantly	instantly
Rotoform	instantly	200	instantly	1
B. Reinforced Papers				
Creped paper	did not absorb	did not penetrate	instantly	13
Kaycel 101-1	instantly	instantly	instantly	2
Kaycel 101-3	3900	did not penetrate	instantly	3
Kaycel RSR-8525	2640	did not penetrate	instantly	3
Chixel	instantly	instantly	instantly	2
C. Laminated Papers				
Kaycel 100, polyethylene coated	did not absorb	did not penetrate	did not absorb	did not penetrate
Disposable rain wear	2820	did not penetrate	did not absorb	did not penetrate
No-Wet-Thru 7502	13	did not penetrate	instantly	did not penetrate
D. Synthetic Fiber Papers				
Masslinn M-840-B	-	-	instantly	instantly
Masslinn RI-750-2209	102	102	instantly	8
Masslinn SI-1300-2110	31	31	instantly	1
Calendered Dacron textryl[b]	instantly	23	instantly	3
Heat-fused Dacron textryl[c]	13	did not penetrate	instantly	9
NONWOVEN FABRICS[d]				
Pellon 970W	instantly	instantly	instantly	instantly
Pellon 717 W	instantly	instantly	instantly	instantly
Pellon 40W	instantly	instantly	-	-
Pellon 901 Nat	instantly	20	instantly	instantly
Pellon 30W	instantly	instantly	-	-
WOVEN FABRICS[e]				
Nylon Style 1181	4	6	instantly	1
Dacron Style 1295	1614	1053	instantly	1
Durado Poplin 3100	did not absorb	did not penetrate	343	120
Cotton Sheeting	instantly	75	instantly	2
FILMS AND FOAMS[f]				
Reynolon 4-6	did not absorb	did not penetrate	did not absorb	did not penetrate
Herculite Micro-Vent	did not absorb	did not penetrate		444
Scott foam	did not absorb	did not penetrate	instantly	1680
Poly(vinyl chloride) film	did not absorb	did not penetrate	did not absorb	did not penetrate
Cellophane[g]	1320	1320	did not absorb	did not penetrate

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[a] The physical properties of these papers were given in Table I-9.

[b] Thickness, 3.9 mils; air permeability, 5.5 ft^3/min/ft^2.

[c] Thickness, 15.9 mils; air permeability, 4.5 ft^3/min/ft^2.

[d] The physical properties of these mat[redacted]

[e] The physical properties of the fabrics were given in Table I-3.

[f] The physical properties of the materials were given in Table I-2.

[g] This was an unplasticized cellophane 0.8 mil thick and weighing 0.3 oz/yd^2.

[redacted]

The poly(vinyl alcohol) film, Reynolon 4-6, the cellophane film, and the poly(vinyl chloride) film resisted the absorption and penetration of the CW simulant. The Herculite Micro-Vent, which is a microporous film containing a scrim, offered little resistance to penetration by the CW simulant. It took 1680 seconds for the simulant to penetrate the polyurethane foam, Scottfoam. All of the films and foams tested, except cellophane, were water resistant. A series of foams having a range of pore sizes were evaluated for resistance to water and a liquid-CW simulant. Single and multiple layers were evaluated. The papers were supplied by the Hollingsworth and Vose Company, The pore sizes of the papers ranged from 20 to 75 microns, and the weights of the papers ranged from 1.7 to 5.5 oz/yd^2. Data on their physical properties and resistance to liquids are given in Table I-35. Single layers of all of the papers were rapidly penetrated by water, and only the paper having a pore size of 20 microns (G-0130) resisted penetration by the CW simulant. Since this paper was the heaviest and thickest in the series, the penetration times of the other papers were redetermined with enough layers of each of the other papers to give approximately the same weight and thickness as G-0130. Under these conditions, all of the papers were resistant to penetration by the CW simulant.

b. Studies of oil- and water-repellent treatments on Kaycel 100

At the time the studies of repellent treatments were started, the development of the reinforced nylon-wood pulp paper that proved to be most suitable for the protective garment was not completed, but it seemed apparent that the best type of material would be a scrim-reinforced paper. Of the readily available commercial products that had been evaluated, Kaycel 100 appeared to most closely approximate the type of material that appeared to be most promising, and it was chosen for the evaluation of finishing treatments.

(1) Comparisons of various treatments

Several series of trials were made to compare different commercial materials for effectiveness in imparting oil- and water-repellent properties to Kaycel 100.

Table I-35. Effect of Pore Size of Paper on Resistance to CW Simulant and to Water[a]

Lot No.	Number of layers	Maximum pore size, microns	Weight, oz/yd^2	Thickness, mils	Air permeability, ft^3/min/ft^2, 0.5 in. water	Penetration time, seconds	
						Water	CW simulant
G-0130	1	20	5.5	36.6	4	290	did not penetrate
G-0486	1	40	3.7	17.2	16	27	15
G-0478	1	60	1.7	7.4	11	6	1
G-0122	1	70	1.4	7.2	29	13	1
W-0307	1	75	1.7	6.6	12	2	1
G-0486	2	40	7.4	34.4	-	290	did not penetrate
G-0478	5	60	8.5	37.0	-	did not penetrate	did not penetrate
G-0122	5	70	7.0	36.0	-	did not penetrate	did not penetrate
W-0307	5	75	8.5	33.0	-	did not penetrate	did not penetrate

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[a] All of the papers were instantly wetted by both water and the CW simulant.

(a) Series 1

Quilon, Quarpel, FC-805 with urea, and FC-805 with Chemigum 245 CHS were compared in the first series. All of the treatments were applied by padding with treating baths and aftertreatments as described below.

Quilon: A bath containing 10% Quilon solids was prepared by dilution at room temperature of 30 parts of concentrated Quilon with 40 parts of water and 30 parts of neutralizing solution (16.5% urea, 5% sodium formate, and 0.2% formic acid). The neutralizing solution raised the pH of the solution from about 2.5 to 3.7. The bath was heated briefly to 95°C to assure hydrolysis of the Quilon chrome complex. It was allowed to cool to room temperature and then applied to give an add-on of 3% solids. The treated material was dried at 95°C for 15 minutes in a circulating air oven.

Quarpel: The Quarpel bath contained 8% Zelan AP and 13.3% FC-154, both on a product basis. The Zelan AP was diluted at 60°C and mixed with 0.8% sodium acetate, following manufacturer's prescribed procedure except that a portion of the water was withheld for dilution of the FC-154. The FC-154 was diluted with warm (40°C) water and added to the solution of Zelan AP. The temperature of the treating bath was 40-45°C during padding and 100% wet pick-up was obtained. The treated material was dried at 120°C for 18 minutes in a circulating air oven and then cured for 3 minutes at 165°C.

FC-805 and urea: Baths were prepared containing 1% FC-805 solids and 1% urea; 3% FC-805 solids and 1% urea; and 1% FC-805 and 8% urea. These baths were applied to give 100% wet pick-up and the treated materials were dried at room temperature.

FC-805 and Chemigum 245 CHS: A bath containing 12.5% Chemigum 245 CHS solids and applied to the material to give 100% wet pick-up was prepared. The treated material was dried at room temperature. The dried material was then treated to give 100% wet pick-up from a bath containing 10% solids consisting of equal parts of FC-805 and urea. The treated material was dried at room temperature.

Data on the water and CW simulant properties of the treated papers are given in Table I-36.

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Table I-36. Resistance of Treated Kaycel 100 to Liquid CW Simulant and to Water

Treatment	Solids add-on, %	Weight, oz/yd²	Thickness, mils	Air permeability, ft³/min/ft², 0.5 in. water	Water		CW simulant	
					Absorption time, sec.	Penetration time, sec.	Absorption time, sec.	Penetration time, sec.
Quilon	3	3.5	9.4	18.5	1341	333	instantly	3
1 part FC-805 + [illegible] part urea	1	2.8	2.9	24.0	3924	did not penetrate	3319	3319
1 part FC-805 + [illegible] parts urea	1	3.3	9.1	23.5	187	187	1886	7649
FC-805 + Chemigum 245 CHS	25[a]	3.3	11.5	10.3	did not absorb	did not penetrate	did not absorb	did not penetrate
[illegible]rpel	8	3.2	9.2	39.5	did not absorb	did not penetrate	did not absorb	did not penetrate

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[a] Equal parts of FC-805 and Chemigum 245 CHS.

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At the concentration level investigated (3% solids), Quilon gave neither water nor CW repellency. The paper containing 1% solids consisting of equal parts of FC-805 and urea was water repellent, and 3319 seconds were required for the CW simulant to penetrate the paper. The paper treated to apply 1% solids add-on of a mixture of 1 part FC-805 and 8 parts urea was not water repellent, but it took 7649 seconds for the CW simulant to penetrate it. Hence, increasing the urea content of the FC-805-urea mixture increased oil repellency. The paper treated with a mixture of equal parts of FC-805 and Chemigum 245 CHS and the paper treated with Quarpel were not penetrated by the CW simulant nor by water after a period of 6 hours.

(b) Series 2

In the second series of trials Quilon, Quarpel, FC-805, and several other products were compared at different add-ons as shown in Table I-39. The treating baths were prepared and the padded papers were aftertreated according to recommendations from the supplier of each product.

A minimum of 4% add-on of Quarpel solids was required to make the Kaycel 100 resistant to penetration by the CW simulant for a period of 6 hours. The treated paper had a spray rating of 100. When FC-805 was substituted for FC-154 in the Quarpel finish, the resulting finish was not effective in imparting CW repellency to Kaycel 100, even at an 8% add-on of solids. The water repellency of the treated papers was also reduced by the substitution.

Alone, FC-805 imparted little if any water resistance to the Kaycel 100. Results for the CW resistance of Kaycel 100 treated with FC-805 were anomalous: samples of Kaycel 100 containing 1 and 4% FC-805 were not resistant; samples containing 3 and 8% FC-805 were CW resistant. The anomalous results probably resulted from nonuniform treatments. A 2% add-on of FC-154 solids made Kaycel 100 both CW and water resistant. The treated paper had a spray rating of 100, and it was not penetrated by the CW simulant at the end of 6 hours. The fluoroalkyl acrylate polymer did not impart CW resistance to Kaycel 100 at add-ons of 1, 2, or 4% solids. At these levels of add-on, the polymer is a poor water repellent.

Table 1-37 Resistance of [illegible] 100 Treated with Oil Repellents or Water Repellents to Liquid CW Simulant and to Water

Treatment	Solids add-on, %	Weight, oz/yd²	Thickness, mils	Air permeability, ft³/min/ft², 0.5 in. water	Hand: Flexibility	Hand: Compressibility	CW simulant: Penetration time, sec.	CW simulant: Absorption time, sec.	CW simulant: Drop behavior[a]	CW simulant: Size of wetted area, mm	CW simulant: Expulsion test, penetration[b]	Water resistance, spray rating
None	-	2.5	5.7	13	pliable	soft	1	<1	4	12		0
Zelan AP + FC-154 (Quarpel)	1	2.8	9.2	35	pliable	soft	960	780	1	5 x 9		70
	2	2.9	9.5	35	pliable	soft	17,640	1,260	1	7 x 7	none	90
	4	2.9	9.8	30	pliable	soft	>>[c]	>>	-	-	none	100
	8	3.1	10.3	27	pliable	soft	>>	>>	-	-	none	100
FC-805	1	2.8	7.8	23	pliable	soft	9,300	>>	1	12 x 9	none	50
	3	2.9	7.9	24	pliable	soft	>>	>>	1	8 x 6	none	0
	4	2.8	8.0	20	pliable	soft	356	136	1	8 x 4	none	0
	8	2.9	8.0	19	pliable	soft	>>	>>	-	-	none	0
FC-154	1	2.9	9.5	24	pliable	soft	>>	10,800	1	-	none	100
	2	2.9	9.0	29	pliable	soft	>>	>>	-	-	none	100
	3	3.0	10.4	28	pliable	soft	>>	>>	-	-	none	100
Zelan AP + FC-805	1	2.7	8.5	28	pliable	soft	4	4	3	7		70
	2	2.8	8.1	32	pliable	soft	9	9	1	6 x 8		70
	4	2.8	8.8	28	pliable	soft	35	35	4	6 x 7		80
	8	2.9	9.0	26	pliable	soft	16	16	1	7 x 5		80
C₇ Fluoroalkyl acrylate polymer	1	2.9	9.0	20	pliable	soft	6	6	4	10		0
	2	2.9	9.1	23	pliable	soft	7	7	4	8		50
	4	2.8	8.6	21	pliable	soft	2	2	4	7		50
Vinylidene fluoride-chlorotrifluoroethylene copolymer	1	2.5	8.3	32	stiff	hard	1	<1	4	10		0
	2	2.6	9.3	37	stiff	hard	2	<1	4	11		50
Vinylidene fluoride-trifluoroethylene copolymer	1	2.5	7.9	20	stiff	hard	4	<1	4	11		50
	2	2.6	8.2	21	stiff	hard	4	<1	4	12		50
Aquapel	2	2.9	8.4	22	pliable	soft	2	<1	4	13		0
Airdex L	4	3.1	10.5	28	pliable	soft	2	<1	4	12		0
Quilon	2	3.0	8.5	24	pliable	soft	1	<1	3	11 x 12		50
	4	3.0	9.3	22	pliable	soft	2	<1	3	14 x 13		50
	8	3.3	9.6	14	pliable	soft	2	<1	3	10 x 10		50
	10	3.5	9.4	17	pliable	soft	2	<1	4	11		0
Permel B	3	3.1	9.3	23	stiff	hard	2	<1	3	9 x 12		80
	4	3.3	11.7	24	stiff	hard	2	<1	3	12 x 13		80
	8	3.5	12.3	15	stiff	hard	2	<1	3	10 x 10		80

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[a]
1. The drops did not wet the material initially, but remain pearled on the surface for various lengths of time and then wet and sink into the sample.
2. The drops wet and sink into the body of the material, but fail to wick out rapidly.
3. The drops immediately enter the material and wick out rapidly, more in one direction than the other to form an elongated pattern.
4. The drops immediately enter the material and wick out rapidly and uniformly in all directions to form a circular pattern.

[b] Made only on samples that show high resistance to penetration and absorption.

[c] Indicates over 6 hours.

The vinylidene fluoride-chlorotrifluoroethylene copolymer was applied to Kaycel 100 from dimethylformamide, and the vinylidene fluoride-trifluoroethylene copolymer was applied to Kaycel 100 from methyl ethyl ketone. Because of the limited solubility of the polymer, add-ons greater than 2% solids could not be obtained. Kaycel 100 containing 1% vinylidene fluoride-chlorotrifluoroethylene copolymer had no CW or water repellency; with 2% of the polymer, no CW repellency and a spray rating of only 50. Kaycel 100 containing 1 or 2% vinyldiene fluoride-trifluoroethylene copolymer had no CW repellency and a spray rating of only 50.

It was envisioned at that time that a multi-layer paper would be used for construction of the overgarment. In a multi-layer system, it is possible that each layer can have a different composition to provide different functional effects. One such system that appeared particularly attractive was an outerlayer that was water repellent and an innerlayer that was CW repellent. A possible advantage of this system was that it would provide protection of the CW-repellent treatment from deterioration by soiling. If the water repellent, outer layer caused the CW agent to spread over a large area, this might be an additional advantage, for there would then be less agent per unit area in contact with the CW-resistant inner layer.

Several water repellents were, therefore, investigated in this series of trials. They were Aquapel (an alkyl ketene dimer), Aridex L (an aqueous dispersion of wax and aluminum soap), Quilon (a chrome complex of a fatty acid), and Permel B (an aqueous dispersion of a melamine resin). At the concentration levels investigated, none of the water repellents gave any CW repellency. The papers containing Aridex L or Aquapel had no water repellency; the Quilon-treated paper had a spray rating of only 50; and the Permel B-treated paper had a spray rating of 80. The treated papers, with the possible exception of the Permel B-treated papers, were not considered sufficiently water repellent for our needs. The Permel B treated papers had the disadvantage of having a harsh, stiff handle. Possibly some of the water repellents studied might have provided satisfactory water repellency at higher levels of add-on, but they would not be suitable for use in the protective overgarment because of the lightweight requirements for the overgarment. The poor results obtained with Quilon are believed to be due to problems in application.

None of the water repellents studied appeared to promote spreading of the CW simulant over a large area of the paper.

(c) Series 3

The papers listed in Table I-12 were evaluated for resistance to water and CW simulant with the results given in Table I-38. Kaycel 101-1 is the same as Kaycel 100, except that it has been treated with a water repellent and flame retardant by the supplier.

All of the latex treatments increased the time required for water to penetrate the impregnated paper. The maximum penetration time, 418 seconds, was obtained with Rhoplex B-15. Some of the latexes slightly improved resistance of the paper to CW simulant; others had no effect. The best resistance to CW simulant, 21 seconds, was obtained with Neoprene 842A.

(d) Series 4

Based on the previous trials and on published information, fluorocarbon chemicals appeared to be most promising for imparting both oil- and water-repellent properties to the paper. Therefore, comparisons were made of five fluorocarbon compounds from Minnesota Mining and Manufacturing Company. The compounds were FC-154, FC-208, FC-805, L-1100, and L-1138. In addition, the Quarpel treatment and the XXCC-3 treatment[16] were also included in the trials. The times of penetration of actual CW agents through Kaycel 100 treated with various repellents as measured by the standard penetration test, are given in Table I-39. The treatments, involving different levels of solid add-on of the several substances, were all carried out by padding with an aqueous bath. FC-208 was the most effective repellent in these trials. With only 2% of FC-208 none of the CW agents penetrated the paper in 6 hours.

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[16] Laboratory Directive No. 112, "Laboratory Impregnation of Fabrics with CC2 by the Aqueous Suspension Process" U. S. Army Chemical Corps Technical Command, Protective Division.

Table I-38. Resistance to Liquid CW Simulant and to Water[a] of Latex-Impregnated Kaycel 101-1

Latex	Water Absorption time, sec.	 Penetration time, sec.	CW simulant Absorption time, sec.	 Penetration time, sec.
None	instantly	instantly	instantly	2
Neoprene 842A	167	167	instantly	21
Rhoplex B-15	418	418	instantly	5
Rhoplex AC-33	108	108	instantly	15
Rhoplex C-72	19	19	instantly	9
Dow Latex 512 K	218	218	instantly	13
Hycar 1572	27	27	instantly	2
Hycar 4501	4	4	instantly	2
Hycar 4501 (40% solids add-on)	4	4	instantly	2

[a] The physical properties of these impregnated papers were given in Table I-12. All of the papers contained 25% latex solids add-on, except where noted.

Table I-39. Penetration Times of CW Agents for Kaycel 100 Treated with Various Repellents

Treatment	Add-on, %	Penetration time, sec.		
		Agent GA	Agent VX	Agent HD
FC-805	0.5	-	3	-
FC-805	2	60	7	a
FC-805	4	60	10	a
Quarpel	2	2,520	300-1200	10,800
Quarpel	4	a	10,800	a
FC-154	2	21,600	a	a
FC-154	3	a	a	a
FC-208	2	a	a	a
FC-208	4	a	a	a
XXCC-3	2	-	3	-
XXCC-3	4	-	3	-
XXCC-3	8	-	3	-
L-110[b]	0.5[c]	-	3	-
L-1138	0.5[c]	-	a	-

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[a] No penetration in 6 hours.

[b] With 0.5% "Zelan."

[c] Applied by Minnesota Mining and Manufacturing Company.

(e) Series 5

Our previous work had shown that impregnation of Kaycel 100 with Rhoplex B-15, an acrylic resin dispersion, imparted excellent flat abrasion resistance. However, the effectiveness of repellent treatments was markedly reduced when the resin dispersion and repellent were applied from the same pad liquor. Consequently, a series of experiments was made in which the Kaycel 100 was impregnated with Rhoplex B-15 and dried 30 minutes at 120°C. Sheets of the resin-impregnated paper were then treated with an aqueous dispersion of FC-208 to provide add-ons of 0.25 to 10%. The results of penetration-time measurements with VX are given in Table I-40. As in the case of Kaycel 100 without Rhoplex B-15, 2% of FC-208 was effective in preventin penetration of the CW agent.

(f) Series 6

The fluorochemical FC-208 is supplied as an emulsion, with a mixed solvent as the external phase. The solvent mixture contains acetone, ethylene glycol, and water in a ratio of 2:1:5, by weight. This solvent mixture can also be used as an extender for the emulsion. However, it is unsatisfactory for use with Rhoplex B-15 impregnated paper, as the solvent has a solubilizing effect on the acrylate resin which results in an undesirable stiff hand of the dried sheet. Water alone is not a desirable extender, for the water-diluted emulsion separates on standin but a water emulsion can be stabilized by adding a small quantity of Phobotex FTC. This effect of Phobotex FTC, a durable textile water repellent, is reported in the literature of the suppliers of FC-208 and Phobotex FTC.

Experiments were made, therefore, to determine the effects of Phobotex FTC on the important properties of the treated paper. Samples of Kaycel 100 containing 25% Rhoplex B-15 were treated with mixtures of FC-208 and Phobotex FTC to gave a 2% add-on of FC-208 and different add-ons of Phobotex FTC. Table I-41 shows the properties of the treated samples, including resistance to penetration by VX. An add-on of more than 0.75% Phobotex FTC decreased the time required for the agent to penetrate the paper.

Table I-40. Time for VX to Penetrate Kaycel 100 Impregnated with 25% Rhoplex B-15 and Various Amounts of FC-208

Add-on of FC-208 solids, %	Penetration time, sec
0.25	120-300
0.5	21,600
1.0	21,600
2	[a]
4	[a]
6	[a]
8	[a]
10	[a]

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[a] No penetration in 6 hours.

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Table I-41. Properties of Kaycel 100[a] Aftertreated with FC-208 and Phobotex FTC

Aftertreatment	Add-on, %	Air permeability, $ft^3/min/ft^2$, 0.5 in. water	Abrasion resistance, cycles to rupture	Water repellency Dynamic absorption method	Water repellency Spray method	Penetration time of VX, sec
FC-208 Phobotex FTC	2 0	13.7	200	36	90	
FC-208 Phobotex FTC	2 0.25	15.5	145	40	100	b
FC-208 Phobotex FTC	2 0.5	13.9	143	38	100	b
FC-208 Phobotex FTC	2 0.75	13.5	188	32	100	b
FC-208 Phobotex FTC	2 1.5	11.5	-	40	-	10,800-14,400

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[a] The Kaycel was treated to apply 25% Rhoplex B-15 solids before treatment with the FC-208 and Phobotex FTC.

[b] No penetration in 6 hours.

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The other properties of this series of samples that were measured were air permeability, abrasion resistance, and water repellency. Water repellency was measured by the dynamic absorption procedure as well as by the spray method. From these data, it appears that the addition of as little as 0.25% Phobotex FTC improved the water repellency, as shown by the spray method. The water absorption values, as measured by the dynamic absorption method, remained about the same. A change of a few percent in the water absorption values is of little significance when dealing with values in the range of 30 to 40%. On the other hand, an increase from 90 to 100 for the spray rating may be a worthwhile improvement in the shedding of water. With increasing amounts of Phobotex FTC, the air permeability remained essentially unchanged while the abrasion resistance appeared to pass through a minimum. In spite of the fact that the abrasion resistance is lowered, it may be desirable to apply 0.25% Phobotex FTC along with the 2% FC-208 to stabalize the pad bath for commercial production.

It was concluded that FC-208 was very effective for imparting water repellency and resistance to VX to paper. The treatment of Kaycel 100 with 25% Rhoplex and 2% FC-208 produced a paper that appeared to satisfy requirements for the overgarment material in regard to both oil and water repellency.

c. Studies of oil- and water-repellent treatments on experimental papers

(1) Effect of fiber content of paper on oil- and water-resistance

The papers that are described in Section III-C-1 were evaluated for resistance to liquid CW simulant, bis(2-ethyl hexyl hydrogen phosphite), and to water with results as given in Table I-42.

Although water did not penetrate the papers containing as little as 25% nylon, the nylon offered little or no resistance to the penetration of the papers by the CW simulant. Papers containing 50% or more of poly(vinyl alcohol) were water resistant, but only the 100%-poly(vinyl alcohol) (PVA) paper showed any significant resistance to penetration by the CW simulant.

Table I-42. Resistance of Experimental Synthetic-Fiber[a] and Wood-Pulp Papers to Liquid CW Simulant and to Water

Type and amount of synthetic fiber	Water		CW simulant	
	Absorption time, sec.	Penetration time, sec.	Absorption time, sec.	Penetratio time, se
None	853	853	instantly	43
100% Nylon	1092	did not penetrate	instantly	21
75% Nylon	1843	did not penetrate	instantly	50
50% Nylon	142	did not penetrate	instantly	2
25% Nylon	194	did not penetrate	instantly	4
100% Poly(vinyl alcohol)	3011	did not penetrate	instantly	146
75% Poly(vinyl alcohol)	283	did not penetrate	instantly	3
50% Poly(vinyl alcohol)	16	did not penetrate	instantly	4
25% Poly(vinyl alcohol)	532	532	instantly	6
50% Cellulose acetate	525	319	instantly	3
25% Cellulose acetate and 25% Nylon	230	298	instantly	2

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[a] The physical properties of these papers were given in Table I-19. All of the papers contained 30% Rhoplex B-15 solids on fiber weight and weighed 3.3 oz/yd^2.

(2) Effects of various scrims in wood pulp and nylon-wood pulp papers

The papers that are described in Section III-C-2 were evaluated for resistance to liquid CW simulant and to water with results as given in Table I-43.

The 4-mesh scrim appeared to decrease the resistance to the CW simulant of the wood-pulp paper, but a 6-mesh or 8-mesh scrim appeared to be slightly beneficial, increasing the respective penetration time 23 seconds and 45 seconds. However, these increases are insignificant compared to the 6-hour protection that is desired. Some of the papers were not penetrated by water, but there is no apparent relationship to scrim structure. The 6-mesh, 100-denier appeared to be the most desirable reinforcement for the papers.

(3) Evaluation of oil- and water-repellent treatments on reinforced 50:50 nylon-wood pulp paper

After the previous studies had shown that the 50:50 nylon-wood pulp paper reinforced with a scrim consisting of 6 x 6 strands per inch of 100-denier nylon yarn was the most promising base paper for the protective garments, studies were made of the effectiveness of oil- and water-repellent treatments on this paper. Handsheets of this paper were made for these studies according to the procedure described in Section III-C-2-b and treated to apply 25% of Rhoplex B-15 solids.

The results of the experiments described in Section III-D-2-b indicated that an aftertreatment to apply 2% FC-208 and 0.25% Phobotex FTC was promising for imparting oil- and water-repellency to papers. This treatment was evaluated for initial effectiveness and for durability of the effects produced when applied to the reinforced 50:50 nylon-wood pulp paper. The treatment with FC-208 and Phobotex FTC was applied as described in Section III-D-2-b.

Table I-43. Resistance to Liquid CW Simulant and to Water of Papers with Scrim Reinforcement[a]

Reinforcement	Strands per in.	Weight, oz/yd^2	Thickness, mils	Water		CW simulant	
				Absorption time, sec.	Penetration time, sec.	Absorption time, sec.	Penetration time, sec.
				Wood-pulp paper			
None	-	3.6	7.8	853	853	instantly	43
Cellulose acetate (100 denier)	4 x 4	4.0	9.8	85	did not penetrate	27	6
Rayon (100 denier)	4 x 4	4.0	10.7	336	did not penetrate	28	10
Nylon (100 denier)	4 x 4	4.0	10.2	491	428	18	8
Nylon (100 denier)	6 x 6	4.1	10.3	274	did not penetrate	315	66
Nylon (100 denier)	8 x 8	4.3	10.1	282	38	333	88
				50% Nylon-50% Wood-pulp paper			
B-62 Rayon scrim	4 x 4	4.0	19.4	657	740	instantly	5
Dixienet cotton scrim	6 x 6	5.2	28.3	1716	1605	instantly	58

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[a] Other properties of these papers were given in Tables I-21 and I-26.

In one experiment a 2 x 6 inch sample was creased along the shorter dimension, by folding it and pressing with a force of 4,400 lb. The penetration resistance of the sample was determined by the usual method, but with the drops of VX placed along the line left by the crease. There was no penetration of the sample within 6 hours.

Another sample was abraded with a Taber abrader for 200 cycles. The abrasion did not reduce the penetration time below 6 hours.

The effect of soiling the surface of the FC-208-treated paper was also investigated. A batch of standard synthetic soil was made according to the formula and method of the American Cyanamid Company.[17] The sample to be soiled was placed on a Crock-Meter and approximately 0.1 g of soil was placed on the sample along a line that would be followed by the reciprocating peg of the Crock-Meter. A piece of 10 oz/yd^2 denim was placed on the peg, and the sample was "crocked" for fifty cycles. The resultant sample, simultaneously soiled and abraded, showed no penetration by VX in 6 hours in the abraded area.

The soiling test was repeated with a paste of 0.1 g of standard soil and 0.2 g of water, instead of the dry soil. Again, there was no penetration by VX in 6 hours.

Two samples of the FC-208 treated paper were subjected to the dynamic water absorption test. One of these samples was dried, while the second one was merely pressed between squeeze rolls, to leave a water content of about 40%. The dried sample was not penetrated by VX in 6 hours; the penetration time of the wet sample varied from 420 seconds to 6 hours.

Samples were also evaluated for resistance to VX by the expulsion test initially and after leaching in water at 30°C for 24 hours. Neither the original nor the leached samples were penetrated. This paper was also resistant to both liquid GA and HD. Furthermore, this paper was not penetrated to either the liquid VX, GB, or HD after it had been stored at 121°C for 96 hours to testing.

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[17] "Soil Resistant Treatment of Fabrics," Textile Finishing Bulletin No. 150, American Cyanamid Company, page 15.

Although the FC-208 treatment imparted water repellency to the reinforced nylon-wood pulp paper, the treated paper was not rain resistant. Rain resistance was not essential for the material to be used in the overgarment, but it was a desired property if it could be obtained without decreasing the CW repellency. The Quarpel-type treatment that was developed by the Quartermaster Corps for producing rain resistance in fabrics was tried for imparting rain resistance to the nylon-wood pulp paper.

Handsheets of the reinforced 50:50 nylon-wood pulp paper that contained 25% Rhoplex B-15 solids were treated with mixtures of FC-208 and Norane R (a pyridinium type water repellent) at different levels of add-on and evaluated for rain resistance at the Quartermaster Research and Engineering Command by AATCC Standard Test Method 35-1961.

The solutions used for treating the papers were prepared by dissolving the Norane R in water at about 75°C, adding 10% sodium acetate on the weight of the Norane R to the solution, and then adding the FC-208. Water was added as needed to adjust the solids contents of the solutions. Solutions were prepared to contain FC-208 and Norane R in the weight proportions of 2:1, 1:1, 1:2, and 1:4. The papers were treated with each of these solutions to apply 4%, 6%, or 8% solids, and the treated papers were dried in a circulating air oven for 4 minutes at 150°C.

All the papers were penetrated by water in the rain test. The lack of rain resistance of the treated papers was probably due to the open structure. A compact paper suitable for obtaining rain resistance would probably have low air permeability and be quite stiff and papery which would make the paper unsuitable for use in the protective overgarment. Because rain resistance was not an essential characteristic of the protective overgarment, no further attempts were made to obtain rain resistance.

(4) Conclusions

Based on these results, it was concluded at this stage of the program that the nylon scrim-reinforced nylon-wood pulp paper bonded with Rhoplex B-15 and aftertreated with FC-208 was a suitable candidate material for fabrication of a light-weight, disposable, protective overgarment.

d. Studies of other methods for obtaining resistance to CW agents

Other methods than oil repellency that were considered for making materials for the protective garment included fiber swelling, gelling, and absorbency. These methods were investigated only very briefly and they did not appear promising.

(1) Fiber swelling

One possible method of inhibiting the passage of liquid CW agents through paper garments is by making the paper from fibers that are easily swollen by the agents. Swelling of the fibers would close the capillaries of the paper and thus retard penetration of the liquid agent. With this thought in mind, the swelling of cellulose acetate, nylon, poly(vinyl alcohol), and wood-pulp fibers in CW simulants was investigated. Each fiber was cut in a Wiley Mill until it passed a 60-mesh screen. One-half gram of the cut fiber was placed in 25 ml of simulant, and the mixture was stirred periodically. After 24 hours, the fibers were decanted and examined visually with a microscope. A small amount of the liquid was evaporated to dryness on a watch glass and any residue was noted. The CW simulants used were bis(2-ethylhexyl)hydrogen phosphite, dibutyl phthalate, and dimethyl hydrogen phosphite.

The poly(vinyl alcohol) (PVA) fiber was swollen by each of the three CW simulants, but there was no evidence of solution. The cellulose acetate fiber was swollen by bis(2-ethylhexyl)hydrogen phosphite and by dibutyl phthalate and was partially dissolved by dimethyl hydrogen phosphite. The other fibers appeared to be unaffected by the simulants.

The swelling of the PVA fiber by bis(2-ethylhexyl) hydrogen phosphite probably explains the slight resistance of the 100% PVA paper to penetration by the CW simulant. For example, 146 seconds were required for the simulant to penetrate a 100% PVA paper and only 43 seconds were required for the simulant to penetrate a 100% wood-pulp paper. Because the swelling of the cellulose acetate fiber and the PVA fiber is very slow, the method did not appear promising.

(2) Gelling and absorbing agents

Several polymers, which it was thought might be useful as gelling agents, were examined for gelling tendencies with three CW agent simulants. The materials that were tried and the observations are given in Table I-44. In these experiments, 2% by weight of the gelling agent was added to the simulant and any swelling or dissolving was observed. The only prospective gelling agent that formed a gel with any of the simulants was carboxymethyl cellulose. High molecular weight poly(vinylpyrrolidone) (PVP K-90) dissolved in dimethyl hydrogen phosphite and increased the viscosity, but it did not form a gel.

Samples of Kaycel 100 impregnated with 25% Rhoplex B-15 solids were treated with carboxymethylcellulose, poly(vinylpyrrolidone) (PVP K-90), poly(vinyl alcohol), or Cab-O-Sil at different levels of add-on. The samples were then evaluated for penetration time with the CW simulant, dimethyl hydrogen phosphite. Also, the area of the drop spread was measured. The data are given in Table I-45. The dimethyl hydrogen phosphite penetrated all the specimens instantly, indicating that none of the gelling or absorbing materials was effective in retarding penetration of the CW simulant. Although the area of the drop spread was altered by the presence of the gelling or absorbing agents, the change in area was not sufficiently great to be beneficial for our purpose.

Samples of Kaycel 100 were also treated to apply both an oil repellent, FC-208, and a gelling or absorbing agent in attempts to get improved resistance to CW agents.

Four samples of Kaycel 100 were brush coated on one side to apply 2 to 4% FC-208. After drying and curing the treated samples, 2% carboxymethylcellulose (CMC) was brush coated on the opposite side of one sample, 5% Cab-O-Sil on another, 5% PVP K-90 on one, and 2.5% PVP K-90 plus 2.5% Cab-O-Sil on the fourth. These samples were evaluated for resistance to penetration by VX. The VX was applied to the side treated with the gelling or absorbing agent. The samples containing carboxymethylcellulose and Cab-O-Sil were not penetrated in 6 hours. One drop of VX penetrated the PVP K-90 treated sample in 20 minutes. The other 4 drops did not penetrate during the 6-hour test period. Two drops of the VX penetrated the sample treated with PVP K-90 and Cab-O-Sil during the 6-hour test period.

Table I-44. Action of CW Agent Simulants on Possible Gelling Substances

Chemical type	Trade name	Dimethylhydrogen phosphite	Dibutyl-phthalate	Bis(2-ethyl-hexyl) hydrogen phosphite
Poly(vinylpyrrolidone)	PVP K-30	soluble	insoluble	insoluble
Poly(vinylpyrrolidone)	PVP K-60	soluble	slightly soluble	slightly soluble
Poly(vinylpyrrolidone)	PVP K-90	soluble	insoluble	insoluble
Vinylpyrrolidone-vinyl-acetate copolymer	PVP/VA W-464	soluble	insoluble	insoluble
Vinylpyrrolidone-styrene copolymer	Polectron 430	insoluble	insoluble	insoluble
Vinylpyrrolidone-styrene copolymer	Polectron 450	insoluble	insoluble	insoluble
Vinylpyrrolidone-ethyl-acrylate copolymer	Polectron 130	insoluble	insoluble	insoluble
Poly(vinyl alcohol)	Elvanol 72-51	soluble	insoluble	insoluble
Carboxymethylcellulose	CMC 70-D high	gel	insoluble	insoluble
Methylcellulose	Methocel 1,500 cps	soluble	insoluble	insoluble
Hydroxyethylcellulose	Cellosize WP-09	soluble	insoluble	insoluble

Table I-45. Effect of Gelling and Absorbing Agents on Area of Drop Spread of Dimethyl Hydrogen Phosphite

Gelling or Absorbing agent	Add-on, % solids	Area of drop spread, mm^2
None		0.95
Carboxymethylcellulose	1	0.64
	2	0.64
Poly(vinyl pyrrolidone) K-90	1	1.32
	2	0.64
	4	0.95
Poly(vinyl alcohol)	1	1.32
	2	1.54
	6	1.13
	10	0.92
Cab-O-Sil	1	1.54
	2	0.95
	6	1.13

In another series of trials, three samples of Kaycel 100 impregnated with Rhoplex B-15 (25% add-on) were brush coated to apply 2 to 4% of FC-208 on one side. After drying and curing, PVP K-90 was brush coated on the opposite side of one sample, carboxymethyl cellulose on another sample, and Cab-O-Sil on the third sample. The add-ons of gelling and absorbing agents were about 1% of all three samples. These three samples along with a sample that had only FC-208 on one face were evaluated for resistance to penetration by VX. The VX was applied to the side treated with the gelling or absorbing agent. The samples with carboxymethylcellulose and Cab-O-Sil showed no penetration during the 6 hour test period. One drop of VX penetrated the PVP K-90 treated sample in 20 minutes; 4 drops of VX at other locations did not penetrate during 6 hours.

Samples of Kaycel 100 impregnated with 25% Rhoplex B-15 solids were treated with 2% carboxymethylcellulose, 2.5% Cab-O-Sil or 2.5% PVP K-90 and then 2% FC-208 was applied over the gelling or absorbing agent. These samples were tested for resistance to VX agent. The samples containing either Cab-O-Sil or PVP K-90 were not penetrated during the 6-hour test period. Two drops of the VX agent penetrated the sample containing CMC in 90 minutes; the other three drops did not penetrate the material during the 6-hour test period.

Even though gelling or absorbing agents may slightly alter the area of the drop spread of CW agents, they apparently diminish the effectiveness of the fluorocarbon treatment. The use of FC-208 appeared to offer a more promising method for making paper resistant to liquid CW agents.

[redacted]

3. Flame retardants

In addition to the protection against liquid CW agents that was needed in the material for the protective overgarment, it would also be desirable that the material be flame resistant, at least enough so to avoid any special hazard when subjected to thermal shock. At the time that the investigation of flame retardants was begun, the most promising material for the overgarment was felt to be a nylon scrim-reinforced 50:50 nylon-wood pulp paper treated with Rhoplex B-15, an acrylic binder, and FC-208, a fluorochemical that imparted CW resistance to the paper. Most of the studies of flame retardant treatments were done with this paper. However, some of the flame retardant treatments were studied on Kaycel 100.

In general, the flame retardant was padded on paper previously treated to apply 25% Rhoplex B-15 solids; but, in some cases, the flame retardant and acrylic binder were applied from a single bath. The flame retardants were applied from aqueous solutions or suspensions by padding to give the desired add-ons, and the treated papers were dried at room temperature. Exceptions to this method are indicated in the discussion of the individual treatments given below.

The most satisfactory of the various flame retardant treatments that were investigated for use on the reinforced nylon-wood pulp paper bonded with Rhoplex B-15 and treated with FC-208 to make it resistant to CW agents was the treatment with tetrakis(hydroxymethyl)phosphonium chloride (THPC) and tris(1-aziridinyl)phosphine sulfide (APS) in a ratio of 1:1. However, the lack of commercial availability and the poor stability of APS made the use of this treatment impractical. No entirely satisfactory method was found for making the candidate paper for the overgarment flame resistant.

a. Treatments applied to Kaycel 100 only

Fourteen flame retardant treatments were applied to Kaycel 100 impregnated with Rhoplex B-15, and several of the retardants were applied to untreated Kaycel 100. The treatments applied to Kaycel 100 and the flame resistance of the treated papers are summarized in Table I-46. At the time of these preliminary evaluations, a char length of 4 inches was considered to be the maximum length consistent with flame resistance. However, flame retardants were considered to be of some value if samples treated with them had char lengths of approximately 6 inches or less.

Table I-46. Flame Resistance of Rhoplex B-15-Bonded Kaycel 100 Paper Aftertreated with Various Flame Retardants

Flame retardant	Weight ratio of components	Add-on of flame retardant, % solids	Flame resistance, char length, in.
Abopan	-	10	consumed
		20	consumed
Fire Retardant L-2	-[a]	10	consumed
Fi-Retard NBX			
applied separately	-	10	consumed
	-	20	5.3
	-	40	4.6
applied with Rhoplex B-15	-	16	4.6
	-	18	4.5
	-	20	4.1
	-	30	4.4
applied with Rhoplex B-15 and 2% FC-208	-	20	4.5
applied with Rhoplex B-15, aftertreated with 2% FC-208	-	20	4.8
applied with 2% FC-208	-	20	4.4
Fi-Retard NBX-carboxymethylcellulose	4 : 0.1[a]	20	4.4
	4 : 0.1	20	consumed
	4 : 0.1	20[b]	consumed
Fi-Retard NBX-poly(vinyl pyrrolidone) K-90	4 : 0.3	20[b]	consumed
Flame Retarder X-12	-	10	consumed
	-	20	consumed
Isano oil	-	11[b]	consumed
	-	20[b]	consumed
Pyroset DO	-	48[a]	4.0
	-	48[b]	consumed
Antimony trioxide-chlorowax 40	-	10-15	consumed
Sb_2O_3-tris(2, 3-dichloropropyl)phosphate	-	10-15	consumed
Borax-boric acid	7 : 3	10-15	3-4
	7 : 3	10	consumed
	7 : 3	20	6.4
DAP-APO	3.6 : 1	23	7.9
Urea-H_3PO_4-formaldehyde-$H_2N\ SO_3H$	4 : 1 : 0.3 : 1	35	consumed
Urea-H_2NSO_3H	1 : 1	33	consumed

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[a] No Rhoplex B-15 on the paper.

[b] Applied from a common bath with Rhoplex B-15 solids.

The methods of preparing the treating baths, applying them to the papers, and curing or drying the treated papers are described below:

Abopan; Fi-Retard NBX; Fire Retardant L-2; Fire Retardant X-12; Sb_2O_3-Chlorowax 40; Sb_2O_3-tris(2, 3-dichloropropyl)phosphate; and borax-boric acid were applied by padding aqueous solutions or suspensions to give the desired add-ons and the treated papers were then dried at room temperature.

Pyroset DO: To 20 g of water was added 10 g of orthophosphoric acid, then 10 g of sulfamic acid in 25 g of water, and last 60 g of Pyroset DO. The bath was applied by padding and the samples were air dried.

Fire Retardant L-2: A 10% solution (product basis) of the Fire Retardant L-2 was prepared. The bath was applied by padding and the samples were air dried.

Isano oil: A solution containing 44% Isano oil was prepared by combining 87.0 g of Isano oil and 10 g of oleic acid with 100 ml of water containing 3.0 g of morpholine and mixing for 2 minutes with a Waring Blendor. Samples were treated by padding and dried at 120°C for 30 minutes.

Urea-orthophosphoric acid-sulfamic acid-formaldehyde: A 76% urea-sulfamic acid-formaldehyde solution was prepared by combining 100 g of urea, 50 g of sulfamic acid, and 50 g of water and heated to 100°C. The solution was cooled to room temperature, and 7.5 g of ammonium hydroxide and 25 g of formaldehyde were added. A 65% urea-orthophosphoric acid-formaldehyde solution was prepared by mixing 100 g of urea and 50 g of orthophosphoric acid and heating to 191°C. The mixture was then cooled to 250°F and 74 g of water, 7 g of ammonium hydroxide, and 10 g of formaldehyde were added. The two solutions were combined to make a solution containing a total of 70% of urea-orthophosphoric acid-sulfamic acid-formaldehyde. The padded samples were cured for 15 minutes at 150°C.

Urea-sulfamic acid: A 66% solution of urea-sulfamic acid was prepared by combining and heating at 82°C for 1 hour, 60 g of urea, 60 g of sulfamic acid, and 20 g of water.[18] The solution was then cooled and 40 g of water was added.

Samples treated with the urea-sulfamic acid solution were cured for 15 minutes at 171°C. The dried samples were washed in warm water, then washed in cool water, and dried at room temperature.

DAP-APO: The diammonium phosphate[19] solution was prepared by dissolving 8.5 g of diammonium phosphate in 121.9 g of water and adding 0.8 g of Triton X-100. Then 38.8 g of APO (85%) was added to the diammonium phosphate solution while stirring vigorously. This solution contained 18.2% APO and 5% diammonium phosphate.

Samples were padded with the DAP-APO solution, dried 2 minutes at 120°C, and then cured 5 minutes at 150°C.

Of these flame retardants, only Fi-Retard NBX imparted sufficient flame resistance (char length <6 inches) to Kaycel 100 treated with Rhoplex B-15. Therefore, Fi-Retard NBX was selected for additional study. In addition to being an effective flame retardant for the wood-pulp paper impregnated with Rhoplex B-15, Fi-Retard NBX was also an effective flame retardant for wood-pulp papers containing 25% solids add-on of Chemigum 245 CHS or Geon 577 as binders. With 40% solids add-on of Fi-Retard NBX, Kaycel 100 impregnated with 25% Chemigum 245 CHS solids or with 25% Geon 577 solids had char lengths of 4.8 inches and 4.3 inches, respectively.

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[18] F. M. Ford and W. P. Hall (to Joseph Bancroft and Sons), U. S. Patent 2,482,756 (1949).

[19] T. D. Miller, F. A. Hoffman, and A. Merala, American Dyestuff Reporter 49, 596-599 (1960).

To keep the cost of processing as low as possible, it would be desirable to apply the flame retardant and the latex binder from the same bath. The flame resistances of samples of Kaycel 100 that were treated by padding Fi-Retard NBX and Rhoplex B-15 from a single bath are also given in Table I-46.with comparable data on samples that were treated by padding the additives from separate baths and drying the samples between the two treatments.

There appeared to be a slight improvement in flame resistance when the flame retardant was applied in the pad liquor with the Rhoplex B-15 rather than applying it to the resin-impregnated paper. Kaycel 100 treated to apply 25% Rhoplex B-15 and 20% Fi-Retard NBX from a single bath had a char length of only 4.1 inches. Moreover, the sample displayed neither afterflame nor afterglow. When Fi-Retard NBX was applied with the Rhoplex B-15 at a concentration level of 16% solids, the treated Kaycel glowed for 5 seconds after the flame went out. It appeared, therefore, that 20% Fi-Retard NBX was about optimum.

It was of course necessary to include a repellent that would prevent penetration of CW agents in the treatment of the paper. As determined previously, FC-208 was effective for this purpose when used alone; and the effect of FC-208 on the flame resistance of Kaycel 100 containing Rhoplex B-15 and Fi-Retard NBX was investigated. The Kaycel 100 was treated with Rhoplex B-15, Fi-Retard NBX, and FC-208 by the following methods: (1) the three additives were applied by padding from a single bath, (2) FC-208 was applied by spraying onto Kaycel 100 impregnated with Rhoplex B-15 and Fi-Retard NBX, and (3) FC-208 and Fi-Retard NBX were applied by padding Kaycel 100 impregnated with Rhoplex B-15. As Fi-Retard NBX was water soluble, it was impractical to pad an aqueous solution of FC-208 onto paper that already contained the fire retardant, for the fire retardant would be washed out of the paper. Thus, Fi-Retard NBX was applied either with other treating agents or as a separate aftertreatment.

The flame resistances of the papers so treated are given in Table I-4 From these results, it was concluded that FC-208 had only a slight adverse effect on the flame resistance of paper containing Rhoplex B-15 and Fi-Retar NBX. FC-208 increased the afterglow from 0 to about 4 seconds, but it did not change the char length significantly. The effect of FC-208 on the flame resistance of the papers was independent of the application methods studied.

When FC-208 and Fi-Retard NBX were applied from the same bath to Kaycel 100 impregnated with Rhoplex B-15, the treated papers had poor resistance to liquid VX agent. As shown previously, when FC-208 and Rhoplex B-15 were applied from a single bath, the treated papers were not resistant to penetration by CW liquids. However, a Rhoplex-impregnated paper aftertreated with FC-208 had very good resistance to CW agents.

A trial was made applying the FC-208 by spraying it on Kaycel 100 containing 25% of Rhoplex B-15 solids and 20% of Fi-Retard NBX solids. A solution of FC-208 was sprayed on the impregnated paper to give 1, 2, or 4% add-on of FC-208 solids. The resistance of the treated paper to penetration by liquid VX agents was generally unsatisfactory and very erratic. With 1% add-on of FC-208 solids, the time required for liquid VX agent to penetrate the treated paper was 90 minutes. With 2% add-on of FC-208 solids, penetration times were 3 to 6 hours; and with 4% add-on, penetration times were erratic, some samples were penetrated in 6 hours, others were penetrated in 1 minute.

On the basis of the studies of flame retardants applied to Kaycel 100, it was concluded that none of the flame retardants evaluated was effective in the presence of the acrylic binder Rhoplex B-15, except Fi-Retard NBX. However, Fi-Retard NBX was not considered satisfactory as a flame retardant for Kaycel 100 treated with Rhoplex B-15 and FC-208 because the treated paper was not resistant to liquid VX agent in the standard drop test.

b. Treatments applied to both Kaycel 100 and 50:50 nylon-wood pulp paper

Flame retardants were evaluated on Kaycel 100 and nylon-scrim reinforced 50:50 nylon-wood pulp papers to which 25% Rhoplex B-15 solids had been applied. In a few instances, the flame retardants were evaluated on the papers not treated with Rhoplex B-15; and, in some cases, in the presence of FC-208. The results of the evaluations are given in Table I-41.

(1) Flame retardants ineffective on Kaycel 100 and 50:50 nylon-wood pulp paper

Four of the eleven flame retardants evaluated in this series of trials were ineffective on both Kaycel 100 and nylon-wood pulp papers containing Rhoplex B-15. These four retardants were: brominated triallyl phosphate (BAP), Pyroset N-2, tris(1-aziridinyl)phosphine oxide (APO), and a mixture of tetrakis(hydroxymethyl)phosphonium chloride (THPC) with Resloom HP.

The treating conditions used were as follows:

BAP: A 33% emulsion of BAP[20] was prepared as follows: 94.5 g of triallyl phosphate and 66 g of bromoform were mixed thoroughly in a flask fitted with a reflux condenser. Then 3.0 g of a 5% solution of Elvanol 71-30 poly(vinyl alcohol) was added. The mixture was stirred continuously with an electric stirrer and 12 g of sodium bicarbonate was added plus about 30 g of water. The mixture was then heated to 82°C and 13 g of potassium persulfate was added along with enough water to bring the total amount of water added to 322 g. The reaction mixture was heated for 2 hours at 82°C and then cooled to 25°C. The pH of the solution was 7.

Samples treated with this BAP emulsion were dried 5 minutes at 85°C, then cured 5 minutes at 140°C. The cured samples were washed once in cool water, rinsed twice in water at 60°C, then rinsed in cool water, and dried at room temperature.

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[20] J. W. Frick, Jr., J. W. Weaver, and J. D. Reid, Textile Research J. 25, 100 (1955).

Table I-47. Flame Resistance of Rhoplex B-15–Bonded Kaycel 100 and 50:50 Nylon-Wood Pulp Papers Aftertreated with Various Flame Retardants

Flame retardant	Weight ratio of components	Paper applied to	Add-on, % solids	FC-208,[a] % solids	Flame resistance, char length, in.
Apex Flameproof 390-B	-	Kaycel 100	15		6.1
	-	Kaycel 100	20		4.9
	-	Kaycel 100	25		3.6
	-	Kaycel 100	20	2P[b]	4.6
	-	Kaycel 100	25	2P[b]	3.2
	-[e]	nylon-wood pulp	25		consumed
	-	nylon-wood pulp	25	2P[d]	consumed
Arzo Fire Retardant 98 B	-[e]	Kaycel 100	15		6.8
	-[e]	Kaycel 100	20		7.2
	-[e]	Kaycel 100	25		5.3
	-[e]	nylon-wood pulp	25		consumed
Brominated triallyl phosphate (BAP)	-	Kaycel 100	20		consumed
	-	nylon-wood pulp	25		consumed
Pyroset N-2	-	Kaycel 100	10		consumed
	-	Kaycel 100	20		consumed
	-	Kaycel 100	50		consumed
	-	nylon-wood pulp	25		consumed
Tris(1-aziridinyl)phosphine oxide	-	Kaycel 100	10		consumed
	-	Kaycel 100	20		consumed
	-[e]	Kaycel 100	20		consumed
	-	nylon-wood pulp	25		consumed
Ammonium sulfamate-diammonium phosphate	7:3[c]	Kaycel 100	10-15		3-4
	7:3	Kaycel 100	10		consumed
	7:3	Kaycel 100	20		4.8
Ammonium sulfamate-diammonium phosphate carboxymethylcellulose	7:3	Kaycel 100	20 2		3.8
Ammonium sulfamate-diammonium phosphate carboxymethylcellulose	7:3	Kaycel 100	20 1		4.2
Ammonium sulfamate-diammonium phosphate carboxymethylcellulose	1:2.6	Kaycel 100	20 2		4.3
Ammonium sulfamate-diammonium phosphate carboxymethylcellulose	1:2.6	Kaycel 100	20 2	2P[f]	consumed
Ammonium sulfamate-diammonium phosphate Cab-O-Sil	7:3	Kaycel 100	20 2		4.5
Ammonium sulfamate-diammonium phosphate Cab-O-Sil	7:3	Kaycel 100	20 1		4.6
Ammonium sulfamate-diammonium phosphate	4:1	nylon-wood pulp	25		consumed
	7:3	nylon-wood pulp	25		4.4
	2:1	nylon-wood pulp	25		6.2
	1:1	nylon-wood pulp	25		6.6
	1:2	nylon-wood pulp	25		6.1
	4:1	nylon-wood pulp	25	2S	6.2
	2:1	nylon-wood pulp	25	2S	6.6
	1:1	nylon-wood pulp	25	2S	6.5
	1:2	nylon-wood pulp	25	2S	5.4
Diammonium phosphate-urea	1:2[c]	Kaycel 100	10-15		3-4
	1:2	Kaycel 100	10		consumed
	1:2	Kaycel 100	20		6.6
	4:1	nylon-wood pulp	25		5.2
	2:1	nylon-wood pulp	25		6.8
	1:1	nylon-wood pulp	25		5.4
	1:2	nylon-wood pulp	25		5.2
	1:4	nylon-wood pulp	25		4.4
	1:4	nylon-wood pulp	25	2S	consumed
Tetrakis(hydroxymethyl)phosphonium chloride and Tris(1-aziridinyl)phosphine oxide	1:1.2	Kaycel 100	10		consumed
	1:1.2	Kaycel 100	20		6.0
	1.1:1	nylon-wood pulp	28		consumed
Tetrakis(hydroxymethyl)phosphonium chloride, Brominated triallyl phosphate, and Resloom HP	1.7:1:1	Kaycel 100	10		consumed
	1.7:1:1	Kaycel 100	20		5.6
	1.7:1:1	nylon-wood pulp	25		consumed
Tetrakis(hydroxymethyl)phosphonium chloride and Resloom HP	1.8:1	Kaycel 100	10		consumed
	1.8:1	Kaycel 100	20		consumed
	4:1	nylon-wood pulp	25		consumed
	2:1	nylon-wood pulp	25		consumed
	1:1	nylon-wood pulp	25		consumed
	1:2	nylon-wood pulp	25		consumed
	1:4	nylon-wood pulp	25		consumed
	1.7:1	nylon-wood pulp	37		consumed
Urea-H_3PO_4	1:1	Kaycel 100	25		consumed
	4:1	nylon-wood pulp	25		consumed
	2:1	nylon-wood pulp	25		consumed
	1:1	nylon-wood pulp	25		consumed
	1:2	nylon-wood pulp	25		consumed
	1:4	nylon-wood pulp	25		6.0

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[a] S = sprayed, P = padded; applied as aftertreatment to paper containing flame retardant.
[b] Padded from a common bath with Apex 390-B to apply 2% FC-208 and 0.25% Phobotex FTC.
[c] No Rhoplex B-15 on the paper.
[d] Padded before the flame retardant was applied.
[e] Padded from a common bath with Rhoplex B-15.
[f] Padded from a common bath with the flame retardant.

Pyroset N-2: Aqueous solutions of the desired concentrations were prepared, and padded samples were dried at room temperature.

APO: A 20% solids solution of APO[21] was prepared by combining 53 g of APO, and 3.0 g of Triton X-100 with 283.4 g of water and then adding 5.6 g of $Zn(BF_4)_2$.

Samples treated with this solution of APO were dried for 5 minutes at 85°C and then cured 5 minutes at 140°C. The cured samples were washed in cool water for 5 minutes, then washed at 60°C for 20 minutes and finally dried at 116°C.

THPC-Resloom HP: A solution of THPC[22] was prepared by dissolving 93.4 g of THPC in 90.0 g of water to which 16.9 g of triethanolamine was added. The Resloom HP solution was prepared by dissolving 53.5 g of Resloom HP and 55.7 g of urea in 156.6 g of water. The THPC solution and the Resloom solution were then combined to make a solution containing 20% THPC and 11% Resloom HP.

Kaycel 100 was treated with THPC-Resloom HP, dried for 5 minutes at 100°C, and then cured 5 minutes at 140°C. The samples were then washed in cool water followed by two rinses in 60°C water. The final drying was done at room temperature.

Solutions of THPC and urea in the proportions of 1:4, 1:2, 1:1, 2:1, and 4:1 by weight were prepared by dissolving the desired amounts of THPC and Resloom HP in 72 parts of water containing 3 parts of triethanolamine to make solutions containing 25% solids. Samples of nylon-wood pulp paper treated with the solutions were dried and cured by the same procedure used for the Kaycel 100 samples.

As shown in Table I-47, all of the samples of Kaycel 100 or 50:50 nylon-wood pulp paper treated with these four flame retardants were consumed in the vertical flame test.

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[21] G. L. Drake, Jr., and John D. Guthrie, Textile Research J. 29, 155 (1951).

[22] W. A. Reeves and J. D. Guthrie, Textile World 104, 101 (1954).

In one trial, Geon 577 (a flame resistant, vinyl chloride resin) was tried as a bonding agent for the nylon scrim-reinforced, nylon-wood pulp paper and antimony oxide was applied with the resin. The amounts of Geon 577 applied was 25% and the amount of antimony oxide was 15% of the weight of the dry paper. The tensile and abrasion resistant properties of the papers with the Geon 577 and antimony oxide were generally comparable to those of papers bonded with 25% of Rhoplex B-15, but the Geon 577-bonded papers were too stiff and harsh to be of use as a material for the protective overgarment.

(2) Flame retardants effective on Kaycel 100 and ineffective on nylon-wood pulp paper

Of the eleven flame retardants evaluated on both Kaycel 100 and 50:50 nylon-wood pulp papers, the seven retardants discussed below were generally effective on Rhoplex B-15 treated Kaycel 100, but ineffective on nylon-wood pulp paper treated with Rhoplex B-15. The data are given in Table I-47.

The treating conditions used to apply the flame retardants to the papers and the results of the evaluations were as follows:

Apex Flameproof 290-B: As shown in Table I-47, Apex Flameproof 290-B was an effective retardant when 25% add-on of solids was applied to Kaycel 100 containing 25% of Rhoplex B-15 solids. The char length of the paper was 3.6 inches. At add-ons of 15 and 20%, the treated paper had char lengths of 6.1 and 4.9 inches, respectively.

Kaycel 100 treated to apply 25% of Rhoplex B-15 and containing solids add-ons of 25% of Apex Flameproof 290-B, 2% of FC-208, and 0.25% of Phobotex FTC applied from the same bath, had a char length of 3.2 inches. However, samples of nylon-wood pulp paper containing 25% of Rhoplex B-15, 2% of FC-208, and 25% of Flameproof 290-B, were consumed in the vertical flame tests. Untreated nylon-wood pulp paper treated with 25% of Flameproof 290-B was also consumed, showing that this flame retardant was not effective for mixtures of nylon and wood pulp.

Akro Fire Retardant 98-B: The char lengths of samples of Kaycel 100 treated with single baths to apply 25% of Rhoplex B-15 solids and 15%, 20%, or 25% of Arko Fire Retardant 98-B solids were 6.8, 7.2, and 5.3 inches, respectively. However, nylon-wood pulp paper treated in the same way to apply 25% of Rhoplex B-15 solids and 25% of Akro 98-B solids was consumed in the vertical flame test.

Ammonium sulfamate (AS)-diammonium phosphate (DAP): Samples of Kaycel 100 padded with a 7:3 AS-DAP mixture to apply 10-15% solids had char lengths of 3 to 4 inches, but samples of Kaycel 100 containing Rhoplex B-15 similarly treated were consumed in the vertical flame test. A 50% solution of ammonium sulfamate and diammonium phosphate was made by mixing 105 g of ammonium sulfamate and 45 g of diammonium phosphate in 150 g of water. Similar baths were also prepared containing 2% carboxymethylcellulose, 1% carboxymethylcellulose, 1% Cab-O-Sil, or 2% Cab-O-Sil.

Kaycel 100 treated with Rhoplex B-15 and 20% AS-DAP had a char length of 4.8 inches, whereas the Kaycel 100 containing similar amounts of Rhoplex B-15 and AS-DAP plus 2% of carboxymethylcellulose only had a char length of 3.8 inches. The addition of 1-2% of Cab-O-Sil to the AS-DAP, however, was not as effective as the addition of the carboxymethylcellulose (CMC). A mixture of AS-DAP (1 : 2.6) and CMC padded on Kaycel 100 containi Rhoplex B-15 to give an add-on of 20% of AS-DAP solids and 2% of CMC solids imparted flame resistance to the paper. However, when the mixture was appli with FC-208 to Rhoplex-treated Kaycel 100 to give an add-on of 22% of the mixture and 2% of FC-208 solids, the treated paper was consumed in the flame test.

Mixtures of ammonium sulfamate and diammonium phosphate in the proportions of 0:1, 1:2, 1:1, 7:3, 2:1, 4:1, and 1:0 were evaluated on 50:50 nylon-wood pulp paper treated to apply 25% Rhoplex B-15 solids. The results are given in Table I-47. The paper treated with the mixture of 7 parts of ammonium sulfamate and 3 parts of diammonium phosphate had a char length of 4.4 inches which was the minimum char length obtained from the various combinations evaluated. This value of char length was about the same as that obtained when diammonium phosphate was used alone (Table I-47).

To determine the effectiveness of the mixtures of ammonium sulfamate and diammonium phosphate in the presence of FC-208, some of the nylon-wood pulp papers containing 25% Rhoplex B-15 solids and 25% of flame retardant mixtures were sprayed with a solution of FC-208 to give an approximate add-on of 2% solids. The ratios of ammonium sulfamate to diammonium phosphate used were 4:1, 2:1, 1:1, and 1:2.

The mixtures of ammonium sulfamate and diammonium phosphate appeared to be as effective on the papers treated with FC-208 as they were on similar papers not treated with FC-208. However, the FC-208 apparently reacted with the diammonium phosphate, for when the papers were sprayed with FC-208, they turned brown and developed a leathery hand. Because of these adverse effects on the appearance and hand of the paper, combinations of ammonium sulfamate and diammonium phosphate did not appear suitable as flame retardants for nylon-wood pulp paper containing Rhoplex B-15.

<u>DAP-urea</u>: Samples of Kaycel 100 without binder padded to apply 10 to 15% of a 1:2 DAP-urea mixture had char lengths of 3 to 4 inches. Rhoplex-treated Kaycel 100 samples treated to apply 10% or 20% of DAP-urea (1:2) solids were consumed and had a char length of 6.6 inches, respectively.

Mixtures of DAP-urea in the ratios of 4:1, 2:1, 1:1, 1:2, and 1:4 were applied by padding aqueous solutions onto Rhoplex-treated 50:50 nylon-wood pulp paper to give 25% solids add-on. The char lengths of the treated papers were 4.4 to 6.8 inches, with the 1:4 DAP-urea mixture being the most effective. However, a sample of the nylon-wood pulp paper treated to apply 25% Rhoplex B-15 and 25% 1:4 DAP-urea and then sprayed to apply 2% FC-208 solids was consumed in the vertical flame test.

THPC-APO: A solution containing 10% of THPC and 10% of APO[23] was prepared by dissolving 30.0 g of THPC in 25.5 g of water containing 7.9 g of triethanolamine, and this solution was combined with a solution containing 35 g of APO, 1.7 g of Triton X-100, and 200 g of water. Samples were treated, dried 5 minutes at 85°C, and cured 5 minutes at 140°C. The cured samples were washed 5 minutes in cool water, washed 20 minutes in warm water (60°C), and then dried at 115°C.

A sample of Rhoplex B-15 treated Kaycel 100 that was padded to apply 10% solids of the 1:1.2 THPC-APO mixture was consumed in the flame test, and a sample with 20% solids add-on had a char length of 6 inches.

A sample of nylon-wood pulp paper treated to apply 25% Rhoplex B-15 and aftertreated to apply 28% of a THPC-APO (1.1:1) mixture was consumed in the vertical flame test.

THPC-BAP-Resloom HP: The THPC-BAP-Resloom HP[24] solution was prepared by combining 81 g of a 33% BAP solution with 230 g of a solution containing 20% of THPC and 11% of Resloom HP. The final solution contained 9% BAP, 15% THPC, and 9% Resloom HP. Samples treated with this solution were dried 5 minutes at 100°C and cured 5 minutes at 140°C. The samples were then washed in cool water, rinsed twice in water at 60°C, and dried at room temperature. At solids add-ons of 10% and 20% of the THPC-BAP-Resloom HP mixture (1.7:1:1), Rhoplex-treated Kaycel 100 samples were consumed and had a char length of 5.6 inches, respectively, in the flame test. Nylon-wood pulp paper treated to apply 25% Rhoplex B-15 and overpadded to apply 25% solids of the THPC-BAP-Resloom HP mixture was consumed in the vertical flame test.

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23. W. A. Reeves, G. L. Drake, Jr., L. H. Chana, and J. D. Guthrie, Textile Research J. 27, 260 (1957).

24. J. D. Reid, J. G. Frick, and R. L. Aveneaux, Textile Research J. 26, 137 (1956).

Urea-orthophosphoric acid: An 18% urea-orthophosphoric acid solution[25] was prepared by dissolving 9 g of urea and 9 g of orthophosphoric acid in 50 g of water. Enough ammonium hydroxide was added to raise the pH to 8.3, and the solution was then diluted to 100 g with water. Kaycel 100 containing Rhoplex B-15 was padded to apply 25% solids of the 1:1 water-H_3PO_4 mixture and then dried for 15 minutes at 150°C. A sample of the treated paper was consumed in the vertical flame test.

Urea and orthophosphoric acid in the proportions of 4:1, 2:1, 1:1, 1:2, and 1:4 by weight were mixed and heated to 88°C. After cooling to room temperature, the mixtures were dissolved in water to make 25% solutions. Samples of Rhoplex B-15-treated nylon-wood pulp paper were padded to apply 25% solids of each of the mixtures and then dried 12 minutes at 150°C. The papers treated with all except the 1:4 mixture burned to the end of the samples, but the sample treated with the 1:4 mixture had a char length of 6.0 inches. All of the mixtures turned the nylon-wood pulp paper brown and increased the stiffness.

(3) Conclusions

The only flame retardants of this group that were found to be effective on 50:50 nylon-wood pulp papers containing Rhoplex B-15 were DAP-urea mixtures and AS-DAP mixtures. However, when 2% of FC-208 was present to provide the necessary CW resistance, the most effective DAP-urea mixture (1:4) did not provide adequate flame resistance and the treated paper sample was consumed in the vertical flame test. Nylon-wood pulp papers containing Rhoplex B-15 and AS-DAP mixtures turned brown and developed a leathery hand when treated with FC-208. Thus, none of the flame retardants discussed in this section was considered satisfactory for use on nylon-wood pulp papers treated with Rhoplex B-15 and FC-208.

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[25] F. M. Ford and W. P. Hall (to Joseph Bancroft and Sons), U. S. Patent 2,482,755 (1945).

c. Treatments applied to 50:50 nylon-wood pulp paper

As mentioned in the introduction to this section on flame retardants, the most promising material for the overgarment appeared to be a nylon scrim-reinforced, 50:50 nylon-wood pulp paper treated to apply 25% of Rhoplex B-15 solids as binder and 2-3% FC-208 solids to provide CW resistance. Thus, much of the investigation of flame retardants was done on this base paper with the Rhoplex B-15 binder, in some cases, aftertreated to apply the FC-208. In the work discussed in this section, unless otherwise noted, the flame retardants were padded on the Rhoplex B-15-treated paper and the treated papers were air dried. Aftertreatment with FC-208 was usually done by spraying FC-208 on the paper containing the flame retardant and then drying and curing the treated paper 6 minutes at 150°C.

A total of 34 flame retardants, singly or in combinations, were evaluated. Thirteen of these retardants imparted sufficient flame resistance to the Rhoplex B-15-bonded nylon-wood pulp paper to warrant investigation of the effectiveness of the flame retardants in the presence of FC-208.

One flame retardant was evaluated on the nylon-wood pulp paper bonded with Geon 577, an aqueous dispersion of poly(vinyl chloride) and a nonflammable plasticizer. A summary of the flame retardant treatments tried and the flame resistances of the treated paper is given in Table I-48 and I-49.

(1) Flame retardant effective on 50:50 nylon-wood pulp paper containing Geon 577

The 50:50 nylon-wood pulp paper was padded with an aqueous dispersion to apply 25% Geon 577 and 15% antimony trioxide solids, dried 30 minutes at 120°C, overpadded to apply 3% FC-208 solids, and then dried 6 minutes at 149°C. The treated paper had acceptable flame resistance (char length 5.5 inches) but was much stiffer than 50:50 nylon-wood pulp paper padded to apply 25% Rhoplex B-15 solids and overpadded to apply 2% FC-208 solids and 0.25% Phobotex FTC.

The resistance to liquid CW agents of the nylon-wood pulp paper treated to apply 25% Geon 577 and 15% antimony trioxide solids and aftertreated to apply 3% FC-208 was determined by the standard drop test. The treated paper was not penetrated by liquid HD, GB, or VX agent.

Although the paper treated with Geon 577 and antimony trioxide was satisfactory in regard to flame resistance and resistance to liquid CW agents, it had poor hand, drape, and flexibility.

(2) Flame retardants effective on 50:50 nylon-wood pulp paper containing Rhoplex B-15

As mentioned above, thirteen of the flame retardants evaluated on Rhoplex B-15-treated nylon-wood pulp paper were sufficiently effective to warrant evaluation of the retardants in the presence of FC-208. Nylon-wood pulp paper containing 25% Rhoplex B-15 solids was padded with aqueous solutions or dispersions of the flame retardants to apply 25% solids, the paper was air dried, sprayed to apply 2% of FC-208 and then dried 6 minutes at 150°C. The treating conditions used with two of the flame retardants were different, and these are given below:

THPC-APS:[23] A treating solution was made by dissolving 35.0 g of THPC, 8.7 g of triethanolamine, 35.0 g of APS, and 2.0 g of Triton X-100 in 119.3 g water, in the order given. The temperature of the solution during the impregnation of the samples was 85-95°C. The treated samples were dried 4 minutes at 85°C and then were cured 5 minutes at 140°C. The cured samples were washed in a cold water bath for 5 minutes, in a hot water bath for 10 minutes, and then rinsed in cool water. The samples were put through a padder to remove the excess water and then dried at room temperature.

Urea-phosphorus pentoxide-formaldehyde:[25] A solution of urea, phosphorus pentoxide, and formaldehyde was prepared by combining 3 parts of urea, 1 part of phosphorus pentoxide, and 2 parts of water and heating the mixture to 95°C. The mixture was cooled to room temperature and 1 part of ammonium hydroxide (28%) and 0.5 part of formaldehyde (37%) were added in that order. Samples were padded with a solution containing 25% solids of the product and dried for 12 minutes at 155°C.

Descriptions of the flame retardants evaluated and the results of vertical flame tests are given in Table I-48.

The three flame retardants used alone were evaluated both in the absence and in the presence of FC-208. For a given flame retardant mixture, only the weight ratio of components which gave the best flame resistance in the absence of FC-208 was evaluated in the presence of FC-208. As shown in Table I-48, samples of nylon-wood pulp paper containing Rhoplex B-15, FC-208, and the following flame retardants were consumed in the flame test: ammonium bromide, ammonium phosphate, 1:2 ammonium bromide-diammonium phosphate, 4:1 ammonium sulfamate-urea, 1:1 Apex 290-B diammonium phosphate, and 3 : 1 : 0.2 urea-P_2O_5-formaldehyde. Samples with the same treatments but without the FC-208 were flame resistant.

Diammonium phosphate was an effective flame retardant in the presence of FC-208 (char length 4.8 inches), but FC-208 apparently reacted with the diammonium phosphate. When the paper was sprayed with FC-208, the paper turned brown and developed a leathery hand. Because of these undesirable effects on the paper, diammonium phosphate was not considered suitable as a flame retardant for the nylon-wood pulp paper.

The remaining six flame retardants imparted sufficient flame resistance to the nylon-wood pulp paper containing Rhoplex B-15 and FC-20 to warrant testing of the treated paper for CW resistance. The effects of th following flame retardants on the CW resistance of the paper were determi

1:1 ammonium bromide-ammonium phosphate
4:1 ammonium bromide-ammonium sulfamate
7:3 ammonium phosphate-ammonium sulfamate
1:1 Apex Flameproof 290-B-Arko Fire Retardant 98B
1:1 Apex Flameproof 290-B-Flameproof Agent 313
1:1 THPC-APS

Table I-48. Flame Resistance of Rhoplex B-15-Bonded 50:50 Nylon-Wood Pulp Paper Aftertreated with Various Flame Retardants that were Effective

Flame retardants	Weight ratio of components	Add-on, % solids	FC-208[a] % solids	Flame resistance, char length, in.
Ammonium bromide	-	25		5.7
	-	33		5.2
	-	25	2S	consumed
Ammonium phosphate	-	25		4.7
	-	25	2S	consumed
Diammonium phosphate	-	25		4.5
	-	25	2S	4.6
Ammonium bromide-ammonium phosphate	4:1	25		5.3
	2:1	25		5.5
	1:1	25		4.7
	1:2	25		6.5
	1:4	25		4.7
	1:1	25	2S	6.0
	4:1	33		5.5
	2:1	33		5.1
	1:1	33		4.1
	1:2	33		4.0
	1:4	33		4.1
Ammonium bromide-ammonium sulfamate	4:1	25		5.5
	2:1	25		consumed
	1:1	25		consumed
	1:2	25		6.3
	1:4	25		consumed
	4:1	25	2S	6.8
Ammonium bromide-diammonium phosphate	4:1	25		5.0
	2:1	25		4.9
	1:1	25		5.4
	1:2	25		4.8
	1:4	25		5.9
	1:2	25	2S	consumed
	4:1	37		5.6
	2:1	37		4.4
	1:1	37		3.5
	1:4	37		4.5
Ammonium phosphate-ammonium sulfamate	4:1	25		6.6
	2:1	25		6.6
	1:1	25		5.6
	1:2	25		5.0
	1:4	25		consumed
	7:3	25		4.8
	7:3	25	2S	4.5
Ammonium sulfamate-urea	4:1	25		5.7
	2:1	25		consumed
	1:1	25		consumed
	1:2	25		consumed
	1:4	25		consumed
	4:1	25	2S	consumed
Apex Flameproof 290-B-Arko Fire Retardant 98 B	1:1	25		consumed
	1:1	40		5.4
	1:1	40	2S	5.5
Apex Flameproof 290-B-diammonium phosphate	4:1	25		6.4
	2:1	25		5.6
	1:1	25		4.1
	1:1[b]	25		3.2
	1:2	25		4.9
	1:4	25		6.8
	1:1	25	2S	consumed
Apex Flameproof 290-B-Flameproof Agent 313	1:1	30		consumed
	1:2	30		5.6
	4:3	35		4.7
	2:1	37		4.4
	3:1	40		4.0
	5:3	40		4.0
	1:1	40		3.8
	3:5	40		4.4
	1:3	40		4.1
	1:7	40		4.6
	1:1	40	2S	6.5
Tetrakis(hydroxymethyl)phosphonium chloride and Tris(1-aziridinyl)phosphine sulfide	1:1	25		5.9
	1:1	25	3P	6.3
Urea-P_2O_5-formaldehyde	3:1:0.2	25		5.3
	3:1:0.2	25	2S	consumed

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[a] S = sprayed, P = padded: applied as aftertreatment to paper [illegible] the retardant.

[b] Contained a small amount of Santomerse 85, a surfactant.

The Apex Flameproof 290-B-Flameproof Agent 313 mixture and the Apex Flameproof 290-B-Arko Fire Retardant 98 B mixture were applied to the Rhoplex-treated paper to give a solids add-on of 40%; the other flame retardants were applied to give a solids add-on of 25%. FC-208 was applied to the paper treated with THPC-APS by padding and to the other papers by spraying. The treated papers were evaluated for resistance to liquid HD, GB, and VX agents by the standard drop and expulsion tests, and the data are given in Table I-49.

The papers treated with Apex Flameproof 290-B-Arko Fire Retardant 98 B, THPC-APS, or Apex Flameproof 290-B-Flameproof Agent 313 had good resistance to the liquid CW agents. The paper treated with Apex Flameproof 290-B-Arko Fire Retardant 98 B was not penetrated by HD or VX agent; its resistance to GB agent was not determined. The paper treated with THPC-AP showed no significant penetrations by any of the agents, and there was only on pin-point penetration by HD agent in the expulsion test. The paper treated wit Apex Flameproof 290-B-Flameproof Agent 313 also showed no significant penetrations by any of the agents; there were only 2 pin-point penetrations by VX agent in the expulsion test. The papers treated with the other 3 flame retardants were penetrated by one or more of the agents.

Of the three flame retardants that had the least effect on resistance to the CW agents, THPC-APS would be preferred because only 25% add-on of the flame retardant was required to give adequate flame resistance. Also since THPC-APS was a durable flame retardant, FC-208 could be applied to the flameproofed paper by padding rather than spraying, which would be required with the other flame retardants. However, as mentioned earlier, APS was not commercially available and its stability is poor. Therefore, the use of THPC-APS treatment was considered impractical.

(3) Flame retardants ineffective on 50:50 nylon-wood pulp paper containing Rhoplex B-15

All of the single flame retardants or mixtures of flame retardants listed in Table I-50 were considered too ineffective to be of interest for treating FC-208 and Rhoplex B-15-treated 50:50 nylon-wood pulp paper. The flame retardants were padded onto the paper from aqueous solutions or dispersions and the treated paper was dried at room temperature. Exceptions to this treating method are noted below.

[redacted]

[redacted]

Table I-49. Resistance of Flameproofed Papers[a] to Liquid CW Agents

Flame retardant	Weight ratio of components	Add-on, % solids	HD			GB			VX		
			Drop test[b]		Expulsion test[c]	Drop test[b]		Expulsion test[c]	Drop test[b]		Expulsion test[c]
			Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated
Ammonium phosphate ammonium sulfamate	7:3	25	0	0	1 (1)[d]	0	0	0	0	0	1
Ammonium phosphate- ammonium bromide	1:1	25	0	0	(2)[d]	0	0	0	0	0	1
Ammonium sulfamate- ammonium bromide	1:4	25	0	0	2	0	0	4	1	3	3
Apex Flameproof 290-B Flameproof Agent 313[e]	1:1	40	0	0	0	0	0	0	0	0	(2)[d]
Apex Flameproof 290-B Arko Fire Retardant 98 B[e]	1:1	40	0	0	0	-	-	-	0	0	0
THPC-APS[e]	1:1	25	0	0	(1)[d]	0	0	0	0	0	0

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[a] Papers contained 25% Rhoplex B-15 solids and 2 to 3% FC-208 solids.

[b] Duration of drop test was 6 hours; 3 specimens were tested with 6 drops per specimen except e.

[c] Duration of expulsion test was 1 minute; 9 specimens were tested with 1 drop per specimen except e.

[d] Numbers in parentheses were pin-point penetrations.

[e] Two specimens with 6 drops per specimen used in drop test; 5 specimens with 1 drop per specimen used in expulsion test.

[redacted]

Table I-50. Flame Resistance of Rhoplex B-15-Bonded 50:50 Nylon-Wood Pulp Paper Aftertreated with Various Flame Retardants that were Ineffective

Flame retardant	Weight ratio of components	Add-on, % solids	Flame resistance char length, in.
Ammonium sulfamate	-	25	consumed
Fire Retardant RC	-	25	6.7
Flameproof Agent 313	-	25	6.7
Pyroset N-10	-	25	consumed
Ammonium phosphate-7:3 borax-boric acid	4:1	25	8.0
	2:1	25	consumed
	1:1	25	consumed
	1:2	25	consumed
	1:4	25	consumed
Ammonium sulfamate-boric acid	1:1	25	consumed
	1:2	25	consumed
	1:4	25	consumed
Ammonium sulfamate-borax-boric acid	1:3.2:1.0	25	consumed
	1:1.6:1	25	consumed
	1:0.8:0.5	25	consumed
	2:0.8:0.5	25	consumed
Ammonium sulfamate-dicyandiamide	4:1	25	consumed
	2:1	25	consumed
Ammonium sulfamate-sodium carbonate	4:1	25	consumed
	2:1	25	consumed
	1:1	25	consumed
	1:2	25	consumed
	1:4	25	consumed
Ammonium sulfamate-thiourea	4:1	25	consumed
	2:1	25	consumed
	1:1	25	consumed
	1:2	25	consumed
	1:4	25	consumed
Apex Flameproof 290-B-Pyroset N-2	2:1	30	consumed
Apex Flameproof 290-B-Pyroset N-10	1:1	30	consumed
Borax-boric acid (7:3)-diammonium phosphate	4:1	25	consumed
	2:1	25	consumed
	1:1	25	consumed
	1:2	25	consumed
	1:4	25	consumed
Borax-diammonium phosphate	2:1	25	consumed
	1:1	25	consumed
	1:2	25	consumed
Diammonium phosphate-ammonium carbonate	4:1	25	consumed
	2:1	25	consumed
	1:1	25	consumed
	1:2	25	6.6
	1:4	25	7.4
Diammonium phosphate-thiourea	4:1	25	8.0
	2:1	25	8.0
	1:1	25	6.5
	1:2	25	6.0
Tetrakis(hydroxymethyl)phosphonium chloride and tris(2-methyl-1-aziridinyl) phosphine sulfide	2.4:1	25	consumed
	1.2:1	25	consumed
	1.2:1	40	consumed
Tetrakis(hydroxymethyl)phosphonium chloride and thiourea	5:1	25	consumed
	2.5:1	25	consumed
	1:1.3	25	consumed
	2.5:1	30	consumed
	2.5:1	40	consumed
Tetrakis(hydroxymethyl)phosphonium chloride and urea	4:1	25	consumed
	2:1	25	consumed
	1:1	25	consumed
	1:2	25	consumed
	1:4	25	consumed
Urea-H_3PO_4-formaldehyde	1:1:0.4	25	6.6

The treating bath of Pyroset Fire Retardant N-10 was prepared by mixing 68.3 g of water, 0.5 g of ammonium chloride, and 31.2 g of Pyroset Fire Retardant N-10 (80% solids) with stirring. Nylon-wood pulp paper treated with Rhoplex B-15 was overpadded with the solution to apply 25% solids add-on and the paper was dried at 170°C for 1 minute.

Urea-orthophosphoric acid-formaldehyde:[18] A mixture of 50 g of urea and 50 g of orthophosphoric was heated rapidly to 150°C, and then cooled and added to a solution of 3.5 g of ammonium hydroxide (28%), and 5.0 g of formaldehyde (37%) in 37.5 g of water. Samples were treated with a solution of the product containing 25% solids and dried 13 minutes at 150°C.

As mentioned in the section above, 1:1 THPC-APS was the most effective flame retardant found for the 50:50 nylon-wood pulp paper containing Rhoplex B-15 and FC-208 that did not adversely affect the CW resistance of the paper. However, the lack of commercial availability and the poor stability of APS made its use impractical. Two alternate compounds, tris(2-methyl-1-aziridinyl) phosphine sulfide (MAPS) and thiourea, were tried as substitutes for APS. The paper used for the evaluations of THPC-MAPS and THPC-thiourea was 50:50 nylon-wood pulp paper containing 25% Rhoplex B-15 solids add-on that was not treated with FC-208.

THPC-MAPS: Samples of the paper were treated with THPC-MAPS in a ratio of 1.2:1 to apply 25% solids. The treating bath also contained 1% of triethanolamine. All samples were dried for 5 minutes at 85°C. Separate samples were cured for 5 minutes at temperatures of 140, 150, 165, and 180°C. All of the treated samples were consumed in the vertical flame test. The same results were obtained with similarly treated samples that were washed 5 minutes in cold water and 10 minutes in hot water after drying and curing.

Samples treated similarly to apply 25% solids of THPC-MAPS in a ratio of 2.4 : 1 or 40% solids of THPC-MAPS in a ratio of 1.2 : 1 and cured for 5 minutes at 140°C had no better flame resistance.

A sample of the nylon-wood pulp paper containing 25% solids add-on of Rhoplex HA-12 and treated similarly to apply 25% solids of THPC-MAPS (1.2 : 1) also showed no flame resistance.

<u>THPC-thiourea</u>: Samples of the nylon-wood pulp paper were treated with THPC-thiourea in ratios of 5 : 1, 2.5 : 1, and 1 : 1.3 to apply 25% solids. The treating baths contained 1% of triethanolamine. The samples were dried 5 minutes at 85°C and cured 5 minutes at 140°C. None of the samples, either washed or unwashed, showed any flame resistance when evaluated by the vertical flame test.

Additional samples were treated to apply 30% and 40% solids of THPC-thiourea (2.5 : 1). Duplicate samples with each treatment were cured for 5 minutes and for 15 minutes. None of the samples showed any flame resistance when evaluated by the vertical flame test.

Thus, none of the flame retardants given in Table I-50 imparted adequate flame resistance to the Rhoplex-treated nylon-wood pulp paper.

E. Experimental Paper 2-2-62

The 3.0 oz/yd^2 nylon-wood pulp paper that was developed in this project (Sections III-C and D) was accepted by the Project Officer as a candidate material for the preparation of the protective overgarment. The material consisted of two 50% nylon and 50% wood pulp sheets reinforced with a nylon scrim treated with an acrylic polymer (Rhoplex B-15) to bond it and increase abrasion resistance and with a fluorochemical (FC-208) to provide water repellency and resistance to liquid HD, GB, and VX.

About 1700 yards of this paper was made in a plant by the Kimberly-Stevens Corporation for laboratory and field evaluations. Prior to the production of this yardage, a trial production run was made to establish the feasibility of making the paper on existing commercial equipment and to determine suitable processing conditions for production.

1. Trial production run

a. Preparation of reinforced paper

One thousand yards of 0.77 oz/yd^2 paper containing 50% of 0.37-inch, 3-denier nylon and 50% Harmac kraft was prepared on a Fourdriner machine, and a scrim containing 6 x 5 strands per inch of 100-denier, high-tenacity nylon was laminated between two sheets of the paper. The preparation of the scrim and the lamination were done continuously on a Kaycel machine— a machine invented by Kimberly-Stevens Corporation. The warp and filling yarns of the scrim were bonded together with polyvinyl acetate (AYAT or equivalent in Solox or acetone), which was applied to the warp yarns. The bonded scrim was coated with a plastisol (Geon 135 in dioctylphthalate) and immediately sandwiched between the paper sheets, and the laminate was dried and hot calendered.

No difficulty was encountered in preparing the base sheet and uniform sheet formation was obtained. During lamination, the base sheet broke frequently at the unwind rolls until the machine could be properly adjusted. When the tension on the unwind rolls was removed, no further breaks occurred and 250 yards of reinforced paper was produced.

b. Treatment of reinforced paper

The reinforced paper was treated with Rhoplex B-15 and then over-padded with FC-208. To establish the process conditions to be used in the plant, a sample of the paper was first treated on a laboratory padder.

(1) Laboratory treatment

A 7-inch wide roll of the reinforced paper was impregnated with Rhoplex B-15 at a speed of 20 ft/min. The paper was passed through a bath containing 31.3% Rhoplex B-15 solids, through one set of hard rubber squeeze rolls at a pressure of 30 psi (which gave 80% wet pickup), and then over Teflon-coated drying rolls heated to 305-310°F. The paper was on the rolls for a total of 1.5 minutes.

The Rhoplex-treated paper was treated with FC-208 on the same machine. The speed of the machine and the temperature of the drying rolls were the same as before. The treating bath contained 2.52% FC-208 solids. Padding was done with only the weight of the squeeze rolls to obtain a wet pick-up of 70%.

During the treatment of the paper with Rhoplex, there was considerable build-up of fibers on the squeeze rolls. No build-up of latex was noted on the drying rolls.

(2) Plant treatment

Approximately 200 yards of the reinforced paper was treated in the plant on a two-roll Butterworth padder and dried by passing it over 40 drying rolls. This paper was designated Experimental Paper No. 1-8-62. The bottom roll of the padder was steel and it dipped into the bath; the top roll was silicone rubber. The treating conditions used are shown in Table I-51.

After each treatment, the treated paper was passed back over the drying rolls. This was to assure complete drying. There was no build-up of fibers on the squeeze rolls as there was in the laboratory treatment.

Table I-51. Plant Conditions for Rhoplex B-15 and FC-208 Treatments

Conditions	Rhoplex treatment[a]	FC-208 treatment[a]
Bath	25-28% Rhoplex B-15 solids	2.86% FC-208 solids
Squeeze roll pressure, psi	24-28	10-14
Wet pick-up, %	100	70
Temperature of drying rolls, °C	120	150
Time of drying, min.	1.5	1.5
Speed, ft/min	150	150

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[a] Material was run over the drying rolls a second time at 100 ft/min. The temperature of the rolls was 150°C.

c. Physical properties of the papers

Table I-52 gives the data on the properties of the base sheet used to prepare the reinforced paper, the laboratory-treated and plant-treated reinforced papers which were made by Kimberly-Stevens Corporation, and, for comparison, a reinforced paper prepared and treated in our laboratory. The base paper used in the plant was made from 50% of 3.0-denier, 0.37-inch nylon and 50% of Harmac kraft; the base paper used in the laboratory was made from 50% of 1.5-denier, 0.25-inch nylon, and 50% International kraft.

Comparison of the properties of the treated papers made at Kimberly-Stevens Corporation shows that the plant-treated, reinforced paper weighed 3.2 oz/yd^2 and the laboratory-treated reinforced paper weighed 2.7 oz/yd^2. Since the same reinforced paper was used for treatment, the difference in weights of the treated papers must have been due to a difference in the amou of shrinkage that occurred and in the amount of solids applied during the treatments. Based on wet pick-up and the solids contents of the impregnati baths, the plant-treated paper contained 25% of Rhoplex B-15 solids and 1.8% of FC-208 solids; and the laboratory-treated paper contained 25-28% of Rhoplex B-15 solids and 2.0% of FC-208 solids. (Unless otherwise stated, th percentages of Rhoplex B-15 are based on the weight of the reinforced paper before impregnation, and percentages of FC-208 are based on the weight of Rhoplex B-15 treated paper throughout the report.)

The laboratory-treated reinforced paper and the plant-treated reinforced paper had about the same breaking strength, elongation at break, stiffness, bursting strength, air permeability, and abrasion resistance. However, the Elmendorf tear strength of the plant-treated paper was over 50% greater than the tear strength of the laboratory-treated paper. The exceptionally high tear strength of the plant-treated paper was partially due to the scrim pulling out of the paper instead of breaking during the determination of the tearing strength. The ease with which the base paper could be separated from the scrim is indicated by the peel strength; and, as shown in Table I-52, the value of peel strength obtained for the plant-treated paper was about half the value obtained for the laboratory-treated paper.

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Table I-52. Properties of Reinforced Nylon-Wood Pulp Papers Made by Kimberly-Stevens Corporation and Southern Research Institute

Description	Weight, oz/yd²	Breaking strength, lb/in.		Elongation at break, %		Elmendorf tear, g		Abrasion resistance, cycles to rupture	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg		Bursting strength, psi	Peel strength, lb/in.	
		Machine	Cross	Machine	Cross	Machine	Cross			Machine	Cross		Machine	Cross
Papers Made by Kimberly-Stevens Corp.														
Base sheet for reinforced paper, untreated 50% [illegible]-denier, 0.37-inch nylon 50% [illegible]mac kraft	0.77	2.1	1.6	3.2	5.3	57.6	73.6	-	185	<4.4	<4.4	2.7	-	-
Reinforced paper[a]														
Laboratory treated[b,c]	2.7	23.5 (16.4)	15.8 (12.3)	21.0 (18.6)	25.5 (26.4)	1555 (1730)	1984 (2547)	192	49	53	24	33	1.05	1.1
Plant treated[b,c,d]	3.2	22.6 (19.4)	16.9 (12.3)	18.6 (19.6)	23.5 (21.1)	3030 (2912)	3056 (2803)	164	56	56	36	56	0.55	0.62
Paper Made by Southern Research Institute														
Experimental paper 8-28-61[c,e]	3.0	34.3 (28.3)		16.3 (25)		1043		200[f]	29	84		81	1.7	

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[a] Paper reinforced with 6 x 5 strands per inch of 100-denier nylon.

[b] Contained approximately 25% Rhoplex B-15 solids on weight of untreated paper and 2% FC-208 solids on weight of Rhoplex-treated paper.

[c] Values in parentheses were determined on samples wet out 1 minute in water.

[d] Experimental Paper No. 1-8-62.

[e] 50% 1.5-denier, 0.25-inch nylon—50% International kraft paper reinforced with 6 x 6 strands per inch of 100 denier nylon. Contained 25% Rhoplex B-15 solids on weight of untreated paper and 2% FC-208 solids on weight of Rhoplex-treated paper.

[f] Did not rupture, 3.4% weight loss after 200 cycles.

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The treated-reinforced handsheets made at Southern Research Institute (designated Experimental Paper No. 8-28-61) weighed 3.0 oz/yd^2 and contained 25% of Rhoplex B-15 solids and 2% of FC-208 solids. The base sheets for the reinforced paper were prepared from 50% of 1.5-denier 0.25-inch nylon and 50% of wood pulp and weighed 1.1 oz/yd^2. The breaking strength, abrasion resistance, bursting strength, and peel strength were higher for the treated-reinforced paper made at Southern Research Institute than for the plant paper; but, the air permeability and tearing strength of the Southern Research Institute paper were lower.

The differences in properties of the papers made in the plant and in the laboratory are attributed to the different nylon fibers that were used in the papers. A 3.0-denier, 0.37-inch nylon was used in the paper prepared in the plant, and a 1.5-denier, 0.25-inch nylon was used in the paper prepared in the laboratory. The 1.5-denier, 0.25-inch nylon was specified for the plant-prepared paper, but the 3.0-denier, 0.37-inch nylon was used by mistake.

2. Production run

Several hundred yards of the reinforced nylon-wood pulp was needed by the U. S. Army Natick Laboratories for field wear evaluations. The ba material for our preferred experimental paper had been prepared from 50% of 1.5-denier, 0.25-nylon and 50% of a semi-bleached kraft pulp made by th International Paper Company. Kimberly-Stevens Corporation did not have either of these fibers in stock and there was not enough time to obtain them for the plant production of the base sheet in time to meet the schedule for th field trials. However, Kimberly-Stevens Corporation had enough materials on hand to prepare a base sheet containing 30% of 3.0-denier, 0.37-inch nylon; 20% of 1.5-denier, 0.25 inch nylon; and 50% of Harmac semi-bleac kraft pulp. Laboratory trials were, therefore, made at Southern Research Institute to determine if a base paper of this composition was suitable for preparing the reinforced paper for field evaluation.

a. Preliminary evaluation of proposed paper composition

Handsheets with the above mentioned composition and, for comparison, handsheets containing 50% of 1.5-denier, 0.25-inch nylon and 50% of International kraft were made in two weights and evaluated. Both the Harmac and the International kraft pulps were beaten to a freeness of 600 Canadian Standard. Data on the physical properties of the papers weighing about 1.2 oz/yd^2 are given in Table I-53. Papers weighing 2.7 oz/yd^2 were treated to obtain an add-on of 25% Rhoplex B-15 solids and dried at 120°C for 30 minutes. The Rhoplex-treated papers were overpadded to apply 2% FC-208 solids and dried at 150°C for 6 minutes. The final weight of these papers was 3.5 oz/yd^2. Data on the physical properties of the treated papers are also given in Table I-53.

The values for the breaking strengths, elongation at break, tearing strength, and bursting strength of the untreated 1.3 oz/yd^2 paper containing 50% of 1.5-denier nylon were slightly higher than those for the untreated 1.1 oz/yd^2 paper containing 20% of 1.5-denier nylon and 30% of 3.0-denier nylon. There were no significant differences in the air permeability or stiffness of the papers.

The treated paper that contained 50% of 1.5-denier nylon had slightly higher wet and dry breaking strength, tearing strength, air permeability, abrasion-resistance, bursting strength, and flexibility than the treated paper containing 20% of 1.5-denier nylon and 30% of 3.0-denier nylon. Both treated papers were resistant to liquid VX agent for at least 6 hours as determined by the standard drop and expulsion tests.

Although the paper containing 50% of 1.5-denier nylon had physical properties somewhat superior to those of the paper containing a mixture of 1.5-denier and 3.0-denier nylon, the latter paper appeared suitable for making the reinforced paper for the field evaluation, and arrangements were made with Kimberly-Stevens Corporation to go ahead with production of this paper for the field evaluation.

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Table I-53. Properties of Nonreinforced Nylon-Wood Pulp Papers Containing 50% of 1.5-Denier Nylon and 50% of Mixed 1.5- and 3.0-Denier Nylon

Description	Weight, oz/yd²	Breaking strength, lb/in.	Elongation, at break, %	Elmendorf tear, g	Abrasion resistance, cycles to rupture	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg	Bursting strength, psi
Untreated								
A. 50% 1.5-denier, 0.25-in. nylon[a] 50% kraft (International)	1.3	3.6	6.0	107	-	122	20	3.6
B. 30% 3.0-denier, 0.37-in. nylon[b] 20% 1.5-denier, 0.25 in. nylon 50% kraft (Harmac)	1.1	2.4	3.3	83	-	120	18	2.4
Treated[c, d]								
A.	3.5	17.4 (13.2)	15.4 (18.0)	672 (707)	151	33	109	54
B.	3.5	15.1 (11.0)	11.6 (16.0)	634 (813)	114	27	186	40

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[a] Base sheet for Experimental Paper No. 8-28-61.

[b] Proposed base sheet for production run.

[c] Papers were treated to apply approximately 25% Rhoplex B-15 solids on weight of untreated papers, and 2% FC-208 solids on weight of Rhoplex-treated papers.

[d] Values in parentheses were determined on samples wet-out for 1 minute in water.

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b. Preparation and treatment of reinforced paper

Kimberly-Stevens Corporation made approximately 1700 yards of the treated, reinforced paper. No difficulties in its production were reported. The base sheet used in the reinforced paper weighed approximately 0.8 oz/yd^2 (30 oz basis weight). The reinforced paper contained 6 x 5 strands per inch of 100-denier nylon yarn and weighed 2.0-2.1 oz/yd^2. It was treated with Rhoplex B-15 to give an add-on of 25% solids and the Rhoplex-treated paper was overpadded to apply 3% of FC-208 solids. The final weight of the paper was 2.6 oz/yd^2. The procedures used were those established in the trial production run which was described earlier in this report. This treated, reinforced paper is referred to as Experimental Paper No. 2-2-62.*

c. Properties of reinforced paper

Data on the properties of the untreated and the treated-reinforced papers are given in Table I-54. Samples of the treated paper were taken from four 425-lb rolls, and the results for each roll are given in the table. Only one sample of untreated paper was evaluated. The data on the properties of the untreated paper are given to provide a basis for comparison with future experimental papers and for control of the properties of this paper in future productions.

As shown in Table I-54, the properties of samples from the different rolls indicated good uniformity of the material. The weight of the treated paper was 2.6 oz/yd^2, which is 0.4 oz/yd^2 lighter than was planned. To obtain a treated-reinforced paper that weighed 3.0 oz/yd^2, we used a base sheet weighing 1.0-1.2 oz/yd^2 in the laboratory. However, we found from the preliminary plant run that an 0.8 oz/yd^2 (30 oz basis weight) base sheet gave a treated-reinforced paper that weighed about 3.0 oz/yd^2; consequently, a base sheet of this weight was made in this plant run. The weight of the treated-reinforced paper prepared was less than expected possibly because of less shrinkage during the finishing treatments.

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* A sample of this paper is included in the Appendix.

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Table I-54. Properties of Reinforced Nylon-Wood Pulp Paper Prepared for Field Evaluation (Experimental Paper No. 2-2-62)[a]

Description	Weight, oz/yd²	Breaking strength, lb/in. Machine	Breaking strength, lb/in. Cross	Elongation at break, % Machine	Elongation at break, % Cross	Elmendorf tear, g Machine	Elmendorf tear, g Cross	Abrasion resistance, % wt. loss after 200 cycles	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg Machine	Stiffness, mg Cross	Bursting strength, psi	Peel strength, lb/in. Machine	Peel strength, lb/in. Cross
Untreated	2.4	14.3 (10.1)	9.6 (7.3)	12.0 (26.6)	12.6 (23.3)	2054	1683	b	29	56	27	37	0.21	0.48
Treated[c]														
Roll 1	3.2	26 (18.8)	20.4 (14.4)	13.3 (18.3)	16.9 (23.3)	1246	2368	3.9	31	36	27	66	0.30	0.37
Roll 2	3.2	26.5 (17.5)	19.5 (14.2)	13.3 (18.9)	20.0 (20.0)	2496	2336	7.9	25	37	41	60	0.51	0.94
Roll 3	3.3	25.3 (17.9)	19.5 (13.9)	14.4 (16.6)	22.2 (20.0)	1802	1258	8.6	38	63	33	56	0.39	1.20
Roll 4	3.2	23.3 (15.7)	17.0 (12.4)	14.4 (13.3)	21.1 (17.7)	2282	1526	8.7	39	77	30	54	0.70	0.75
Average	3.2	25.3 (17.5)	19.1 (13.7)	13.9 (16.8)	20.1 (20.3)	2237	1872	7.3	32	53	32	59	0.50	0.80

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[a] Papers were prepared by Kimberly-Stevens Corporation. Values in parentheses were determined on samples wet out 18 hours in water.

[b] Ruptured at 54 cycles.

[c] Contained approximately 25% Rhoplex B-15 solids on weight of untreated paper, and 3% FC-208 solids on weight of Rhoplex-treated paper.

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Compared to the treated paper prepared in the trial plant run (Experimental Paper No. 1-8-62), the dry breaking strength, bursting strength, and abrasion resistance of this paper (Experimental Paper No. 2-2-62) were slightly higher; the wet breaking strength, stiffness, and peel strength of the two papers were about the same; and the tearing strength and air permeability of the 2-2-62 paper were lower. These differences in properties may have resulted from the larger amount of the 3.0-denier nylon in the 1-8-62 paper. The 1-8-62 paper contained 50% of 3.0-denier nylon; the 2-2-62 paper contained 30% of 3.0-denier nylon and 20% of 1.5 denier nylon. Greater differences in the properties of the papers might have resulted if the papers had weighed the same—the 2-2-62 paper was 0.6 oz/yd^2 lighter than the 1-8-62 paper. The 2-2-62 paper was not as white as the 1-8-62 paper, and it had a greasy hand that the 1-8-62 paper did not have. Both of these last differences may have been due to the larger amount of FC-208 on the 2-2-62 paper.

Compared to the reinforced-nylon wood pulp paper prepared and treated in the laboratory (Experimental Paper No. 8-28-61), paper 2-2-62 had lower breaking strength, elongation at break, and bursting strength. The air permeability and abrasion resistance of the papers were about the same. The plant paper had higher tearing strength and better flexibility and drape. These differences in properties might also have been caused by the different nylons used in the paper or the difference in the weight of the papers.

3. CW resistance of Experimental Paper No. 2-2-62

The resistances of Experimental Paper No. 2-2-62 to liquid HD, GB, and VX agents, as determined by the standard drop and expulsion tests, are given in Table I-55. Twenty-one specimens were randomly taken for evaluation from each of 4 rolls of the paper. Six of the specimens were used for the drop test (2 for each agent) and 15 of the specimens were used for the expulsion test (5 for each agent). In the drop test, 6 drops of an agent were used for each specimen; in the expulsion test, only one drop of an agent was used for each specimen. The results are given for each roll of paper. Pin-point penetration is usually considered insignificant but is reported here.

As shown in Table I-55 only one of the 84 specimens evaluated failed to give satisfactory resistance to the agents. One specimen out of 5 was penetrated by a drop of VX agent in the expulsion test. However, two specimens showed pin-point penetrations in the expulsion tests with VX agent and half of the specimens showed pin-point penetrations in the drop tests with HD agent. There was no penetration of any specimens by HD in the expulsion test, by GB in the drop test or expulsion tests, or by VX in the drop test.

In tests at the Army Chemical Center,[26] Experimental Paper No. 2-2-62 showed no significant penetration of the paper by HD, GA, GB, or VX agents in the drop test at the end of the 6 hours. Some pin-point penetrations of the paper were noted with the HD and GA agents, but not with the GB and VX agents. In the expulsion test, there was no penetration by any of these agents after 30 seconds, the duration of the test. Samples of the paper taken from the knees of garments that had been field evaluated still showed good resistance to the agents. These results are summarized in Table I-56.

4. Field evaluation of Experimental Paper No. 2-2-62

Experimental Paper No. 2-2-62 was field evaluated in overgarments by the U. S. Army Natick Laboratories at Maynard, Massachusetts, under wet-cold conditions and at Fort Lee, Virginia, under dry-cold conditions. The trials were carried out over rough terrain at a low level of combat activity. The trials at Maynard were for a duration of 3 hours and Figure I-1 depicts participants during the evaluations at Maynard. In the trials at Fort Lee, Virginia, the garments were taken from the test as soon as a failure was noted. A representative of Southern Research Institute observed the field trial at Maynard, and a representative of International Latex Corporation observed the field trials at Fort Lee.

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[26] Letter of April 9, 1962, from Mr. Marshall Gilchrist to W. C. Sheehan.

[redacted]

Table I-55. Resistance of Experimental Paper No. 2-2-62 to Liquid CW Agents

Roll number	VX			HD			GB		
	Drop test[a]		Expulsion test[b]	Drop test[a]		Expulsion test[b]	Drop test[a]		Expulsion test[b]
	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated
1	0	0	1	1	(5)[c]	0	0	0	0
2	0	0	0	1	(2)	0	0	0	0
3	0	0	0	1	(1)	0	0	0	0
4	0	0	(2)	1	(1)	0	0	0	0

[a] Duration of drop test is 6 hours; two specimens tested, each with 6 drops of agent; 7 to 8 mg drops.

[b] Duration of expulsion test is 1 minute; five specimens tested, each with 1 drop of agent, 7 to 8 mg drops.

[c] Numbers in parentheses are pin-point penetrations.

[redacted]

Table I-56. Resistance of Experimental Paper No. 2-2-62 to Liquid CW Agents as Determined by Army Chemical Center[a]

Material	Drop test[b]						Expulsion test[c]	
	Time, hr	Tests	HD	GA	GB	VX	Time, sec.	Results
New	1	5	0	0	0	0	30	no penetration by any agent
	2	15	0 (1)	0 (5)	0	0		
	6	15	0 (3)	0 (11)	0	0		
Worn	1	4	0	2 (2)	0 (2)	0 (1)	15	no significant penetration by any agent. Very soiled and worn material gave few pin-points of penetration with GA.
	3	4	1	0 (3)	0	0		
	6	4	0 (1)	1 (2)	0 (1)	1		
							30	less than 0.5 mg penetration of all agents on very soiled and worn swatches. No penetration on wrinkled and slightly soiled swatches.

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[a] Letter of April 9, 1962, to W. C. Sheehan.

[b] Number of significant penetrations. Figures in parentheses are the numbers of insignificant pin-point penetrations.

[c] Tests in triplicate.

Figure I-1. Field Evaluation of Experimental Paper No. 2-2-62, at Maynard, Massachusetts.

Number of significant penetrations. Figures in parentheses are the numbers of insignificant pin-point penetrations.

c Tests in triplicate.

The results of these trials were reported in detail by the Quartermaster Corps; hence, only a summary of the findings are given here.

- The paper was estimated to have a service life of about 3 hours under wet conditions and about 4 hours under dry conditions.[27]

- Failures of the paper under the wet conditions were due principally to wet abrasion and to snagging (or puncture).

- Failures of the paper under the dry conditions were due principally to snagging and delamination. The abrasion resistance was decidedly better dry than wet, and when double layers of the paper were used at knees and elbows the test garments went through the trials without wear-through.

- The overgarments lasted longer when the load carrying equipment was over the garment, rather than under it.

- Glued seams made with Splic-It Adhesive were satisfactory under both wet and dry conditions. Ultrasonically-sealed seams made under the best conditions were about as good as the glued seams under dry conditions, but they failed under wet conditions.

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[27] Meeting with Mrs. Mary Darby of the U. S. Army Natick Laboratories, April 4 and 5, 1962, in Birmingham, Alabama.

F. Studies to Overcome Deficiencies of Experimental Paper 2-2-62

The physical properties of the candidate paper that most needed to be improved, as shown by the results of the field trials, were wet abrasion resistance, puncture (or snag) resistance, and adhesion of the base sheets to scrim. Binders, increased paper weights, and scrim adhesives were investigated for improving these properties.

1. Scrim adhesives

a. Pilot-plant studies

One problem encountered in the field evaluation of the plant-produced Experimental Paper No. 2-2-62 was delamination. In the production of the reinforced papers by Kimberly-Stevens, an unwoven scrim was made by bonding warp yarns treated with a polyvinyl acetate adhesive to filling yarn The bonded scrim was then coated on both sides with another adhesive, call a filling or scrim adhesive, to bond the paper sheets to it. The scrim adhesive in Experimental Paper No. 2-2-62, which will be referred to as Adhesive KS-1, was a polyvinyl chloride plastisol (Geon 135 in dioctyl phthalate).

Our studies showed that Splic-It, EC-1729, and SC-377 were good adhesives for the nylon scrim, and samples of these materials were sent to Kimberly-Stevens to determine whether they could be used on their production equipment. Kimberly found that Splic-It and EC-1729 could be used, and reinforced nylon-wood pulp papers were prepared with them and with an organosol (a mixture of 85% adhesive KS-1 and 15% mineral spirits), which will be referred to as Adhesive KS-2. A bonded scrim, which contained polyvinyl acetate adhesive on the warp yarns, was coated with Adhesive KS-2 on one side, and the coated scrim was laminated betwee sheets of the base paper used for making Experimental Paper 2-2-62. The amounts of adhesive applied to the scrim, the peel strengths of the reinforce papers, and the peel strength of the paper that was field evaluated (2-2-62) are given in Table I-57.

Table I-57. Peel Strengths of Nylon-Wood Pulp Papers Reinforced with Nylon Scrim Treated with Various Adhesives[a]

Adhesive	Adhesive weight on yarns, g/yd²		Peel strength, lb/in.	
	Warp	Fill	Machine	Cross
KS-1[b]	4-6	16-18	0.5	0.8
EC-1729	c	c	0.8	0.7
KS-2	3.0	10.1	0.8	1.5
Splic-It	3.2	8.8	1.1	1.0

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[a] All scrims contained poly(vinyl acetate) on the warp yarns to bond the scrim. The bonded scrim was coated on one side with adhesive. The laminate was treated to contain 25% Rhoplex B-15 solids on weight of untreated paper and then overpadded with 3% FC-208 solids.

[b] Geon 135 in dioctylphthalate.

[c] Weight not determined.

The highest peel strength obtained (1.5 lb/in.) was in the cross direction of the paper containing the KS-2-treated scrim. However, the peel strength of this paper in the machine direction was only about half this value. The peel strengths of the paper containing Splic-It were about 1 lb/in. in both the machine and cross directions. With EC-1729, peel strengths of only about 0.7 lb/in. were obtained, and with the KS-1 a value of only 0.5 lb/in. was obtained in the machine direction of the paper. As a result of the good peel strengths obtained with Splic-It and Adhesive KS-2 it was decided that plant runs would be made at Kimberly-Stevens with these adhesives.

b. Plant trials with Splic-It and Adhesive KS-2

A scrim with 6 x 5 strands per inch of 70-denier, high tenacity nylon yarn and bonded by polyvinyl acetate on the warp yarns was coated on both sides with the scrim adhesive and then laminated between two sheets of the base paper used for making Experimental Paper No. 2-2-62. The peel strengths of papers made with two amounts of Splic-It and of papers made with two amounts of Adhesive KS-2 are given in Table I-58.

The peel strengths of these papers were considerably lower than those obtained when the same adhesives were used in the pilot-plant studies. This difference was attributed to the use of a scrim made of 100-denier nyl yarn in the pilot-plant studies and the use of a scrim made of 70-denier nyl yarn in the plant studies. The scrim made from 70-denier nylon yarn was used in the plant studies, because it was being made on the plant equipment at the time that the studies were made. Nevertheless, the results of the pl studies confirmed the results of the pilot-plant studies, namely that Splic-It was somewhat more effective than Adhesive KS-2 for producing papers with high peel strength. However, Kimberly-Stevens found that Splic-It was not suitable for use on their plant equipment because of the mechanical instabil of the latex. Splic-It left solid resin in the lines of the equipment that was very difficult to clean out. Consequently, our efforts in the laboratory were directed to determination of the optimum conditions for producing high peel strength papers with Adhesive KS-2 as the scrim adhesive.

Table I-58. Peel Strengths of Nylon-Wood Pulp Papers Reinforced with Nylon Scrims Treated with Various Adhesives[a]

Scrim adhesive	Adhesive weight,[b] scrim, g/yd^2		Peel strength, lb/in.	
			Machine	Cross
KS-2 (organosol)	18.5	(0.9)	0.40	0.75
KS-2 (organosol)	9.5	(0.47)	0.25	0.55
Splic-It	9.5	(0.47)	0.40	0.55
Splic-It	5.2	(0.26)	0.4-0.7	0.45

Trials made at Kimberly-Stevens on May 8, 1962.

Values in parentheses are the add-ons in grams/8 x 8-inch sample to provide a direct comparison with values in Table I-59.

c. Laboratory studies with Adhesive KS-2

The factors that were investigated for obtaining the maximum peel strength of papers with Adhesive KS-2 as the scrim adhesive were: amount of adhesive, curing time, curing temperature, and pressure during curing.

The scrims used for this study were made with 6 x 6 strands per inch of 100-denier nylon yarn. They were made on a pin frame, and the adhesive was applied to both sides with a brush. Immediately after applying the adhesive, paper handsheets (50:50 nylon-wood pulp) were placed on both sides of the scrim (still under tension on the pin frame), and the laminate was put in a heated press. The laminates were held in the press at various pressures and temperatures and for various periods of time. The lamination conditions and the peel strengths of the papers are given in Table I-59.

The peel strengths of the scrim-paper laminates were determined with a Scott IP-4 machine.

Based upon these results, the conditions recommended for lamination with Adhesive KS-2 were as follows: minimum adhesive add-on of 24-28 g/yd^2; minimum curing temperature of 135°C; and minimum curing time and pressure of 1 minute and 50-100 psi.

2. Increased paper density

Increased paper density was investigated as a means of improving the puncture (or snag) resistance of the paper for the overgarment. Nylon-wood pulp handsheets of equal weights but of different thicknesses were prepared, and the puncture resistance and air permeability of each paper were measured. As shown in Table I-60, an increase in density of the paper increased puncture resistance, but it also greatly decreased air permeability.

3. Increased weight of paper

To determine what effect increased weight would have on the properties of the candidate paper, papers that weighed 3.0, 3.6, and 3.9 oz/yd^2 were prepared and their properties were evaluated.

Table I-59. Peel Strengths of Nylon-Wood Pulp Papers Reinforced with a Nylon Scrim That Was Treated with Adhesive KS-2

Adhesive add-on, g[a]	Curing conditions: Temperature, °C	Curing conditions: Time,[b] min.	Curing conditions: Pressure, psi	Peel strength,[c] lb/in.
1.0	150	1	500	0.4-0.6
1.4	150	1	300	0.4-2.1 variable
1.2	150	1	300	1.0
1.2	150	1	100	>3.4
0.6	150	1	100	0.6
1.2	135	1	100	>3.4
1.2	135	1	100	>3.4
1.1	135	1	100	>3.4
0.8	135	1	100	1.2
0.6	135	1	100	0.5
1.0	120	1	100	0.4
0.9	95	1	100	0.25
1.4	135	0.5	100	>3.4
1.2	135	0.5	100	>3.4
1.4	120	0.5	100	>3.4
1.2	120	0.5	100	>3.4
1.2	120	0.5	100	>3.4
1.4	95	0.5	100	0.5
1.2	95	0.5	100	0.4
1.2	120	0.5	50	>3.4
1.2	120	0.5	50	>3.4
1.2	120	0.5	25	0.25
1.2	120	0.5	25	0.25[d]

---

[a] On 8 x 8 inch sheet (to convert to g/yd^2, multiply by 20.25) of 50% 1.5 denier, 0.25-inch nylon and 50% International kraft fibers.

[b] In closed press.

[c] >3.4 indicates that the bond was stronger than the paper.

[d] Small areas of the sheet had peel strength >3.4.

Table I-60. Effect of Paper[a] Density on Puncture Resistance and Air Permeability

Paper, weight,			
g	4.0	4.0	4.0
oz/yd^2	2.9	2.9	2.9
Paper thickness, mils	15.2	8.4	7.7
Paper density, g/cc	0.259	0.471	0.513
Puncture strength, lb	3.31	4.62	4.92
Air permeability, ft^3/min/ft^2, 0.5 in. water	14.5	1.37	1.25

---

[a] Untreated 8 x 8-inch handsheets containing 50% of 1.5-denier, 0.25-inch nylon, and 50% of semi-bleached International kraft fibers with no scrim.

The base sheets used in these papers contained 50% of 1.5-denier, 0.25-inch nylon and 50% of wood pulp. The weights of the base sheets were increased proportionally so that after reinforcement with the scrim and aftertreatment of the reinforced paper with Rhoplex B-15 and FC-208 the final weights were 3.0, 3.6, and 3.9 oz/yd^2. The papers were reinforced with a 6 x 6 scrim of 100-denier nylon containing 100% Splic-It on the weight of the scrim, and the reinforced papers were treated to apply 25% of Rhoplex B-15 solids. The impregnated paper was treated to apply 2 to 3% FC-208 solids.

The data for the abrasion resistance, puncture strength, air permeability, and bursting strength of each paper are given in Table I-61. As expected, the abrasion resistance (wet and dry), puncture strength, and bursting strength of the paper increased with increased weight, and the air permeability decreased. It was concluded from these data that a small increase in the weight of the base sheet used in the reinforced paper markedly improves the durability of a nylon-wood pulp paper.

4. Binder studies

Attempts were made to increase the wet abrasion resistance of the nylon-wood pulp paper by the use of acrylic latex binders.

a. Hycar 260-92 and Hycar 200X-30

The base paper used for making Experimental Paper No. 2-2-62 was used for these studies. One set of samples of the paper was treated with Hycar 260-92, a self crosslinking acrylic latex, to give an add-on of 25% solids. A second set of samples was treated with a 2.5 : 1 (solids) mixture of Hycar 200X-30, an acrylic latex that is crosslinked by melamine resins, and Aerotex M-3, a melamine formaldehyde resin, to apply 35% total solids. The treated samples were dried at 95°C and cured 3 minutes at 150°C. As a control, samples of the paper were treated to apply 25% of Rhoplex B-15 solids and the treated samples were dried for 30 minutes at 120°C. All three sets of samples were overpadded to apply 3% of FC-208 solids and dried 6 minutes at 150°C. The properties of the treated papers are given in Table I-62.

Table I-61. Properties of Reinforced Nylon-Wood Pulp Papers of Different Weights[a]

Weight, oz/yd^2	Abrasion resistance, cycles to rupture, surface layer		Puncture strength, lb	Air permeability, ft^3/min/ft^2, 0.5 in. water	Bursting strength, psi
	Dry	Wet			
3.0	91	38	5.7	29	81
3.6	118	58	7.9	29	100
3.9	167	70	8.6	15	111

---

[a] Treated to contain 25% Rhoplex B-15 solids on weight of untreated paper, and then overpadded with 3% FC-208 solids.

Table I-62. Properties of Reinforced Nylon-Wood Pulp Paper[a] Treated with Various Latexes

Latex treatment	Weight, oz/yd²		Breaking strength, lb/in.		Elongation at break, %		Elmendorf tear, g		Abrasion resistance, cycles to rupture surface layer	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg		Bursting strength, psi	Puncture strength, lb
			Machine	Cross	Machine	Cross	Machine	Cross			Machine	Cross		
Rhoplex B-15[b]	3.3	dry	20.9	18.6	22.1	22.3	2464	2688	108	43	80	91	65	4.1
		wet[c]	15.5	14.3	26.0	25.5			90					
Hycar 260-92[b]	3.3	dry	22.1	18.3	26.6	24.6	2636	2582	77	33	60	89	62	3.9
		wet[c]	16.3	14.6	29.0	27.6			68					
Hycar 2600X-30 and Aerotex M-3[d]	3.5	dry	24.1	18.5	24.1	21.0	2374	1568	121	35	47	58	65	4.0
		wet[c]	17.6	14.8	27.2	24.5			57					

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[a] Base papers from production of Experimental Paper No. 2-2-62.

[b] Paper treated to apply 25% latex solids on weight of untreated paper, and then impregnated paper was overpadded with 3% FC-208 solids.

[c] Soaked in water 18 hours.

[d] Paper treated to apply 25% Hycar 2600X-30 solids and 10% Aerotex M-3 solids on weight of untreated paper and then impregnated paper was overpadded with 3% FC-208 solids.

The crosslinked Hycar resins did not increase the wet abrasion resistance and increased the wet breaking strength of the paper only slightly compared to Rhoplex B-15.

b. Rhoplex B-15, Rhoplex HA-8, and Rhoplex HA-12

Nylon-wood pulp handsheets made in our laboratory were used for these evaluations. The handsheets were not laminated with a scrim. Samples of the handsheets were treated with Rhoplex B-15, Rhoplex HA-8 and Rhoplex HA-12 in combination with Rhonite 401 (a crosslinking agent) and in the presence of various catalysts: Catalyst A, zinc nitrate plus acetic acid, oxalic acid, and ammonium chloride. The treated samples were dried, cured, overpadded to apply 3% FC-208 solids, again dried, and cured. The treating materials, the treating conditions, and the results of abrasion resistance measurements on the treated papers are given in Table I-63. The best wet abrasion-resistance value was obtained for the paper which was: (1) treated with Rhoplex HA-12 and 0.5% of Catalyst A (based on the bath weight) to apply 25% resin solids and cured 5 minutes at 150°C, and (2) overpadded to apply 3% solids of FC-208 and cured 3 minutes at 150°C.

5. Dyeing

One of the requirements for the overgarment material was that it be an OD shade. Dispersed pigments appeared to be most suitable as coloring agents, and several combinations of pigments were investigated in efforts to produce a satisfactory OD color without interfering with other properties of the nylon-wood pulp papers.

The experimental results described in Section III-D-3-c of this report indicated that Rhoplex HA-12 was the most promising acrylic binder for the paper and earlier results had shown that the Geon 577 and antimony trioxide combination was promising for producing a flame resistant paper without impairing resistance to CW agents although it produced an undesirable hand. Therefore, studies of dyeing methods were directed toward those which could be used with both of the above binder systems. The paper used in these dyeing studies was the laminated but untreated sheet made at Kimberly-Stevens for the production of Experimental Paper No. 2-2-62.

Bath									Overtreatment				
Resin		Additives		Drying conditions		Curing conditions			Drying and curing		Abrasion resistance,[c] cycles to rupture	
Rhoplex	Approximate add-on, %[b]	Material	% on bath	°C	Min	°C	Min	% FC-208	°C	Min	Wet	Dry
B-15	20	-	-	120	30	-	-	3	150	6	8	80
B-15	25	-	-	120	30	-	-	3	150	6	17	65
B-15	30	-	-	120	30	-	-	3	150	6	11	-
B-15	25	Rhonite 401	5.0	65	10	150	10	3	150	6	33	126
B-15	25	Oxalic acid	0.05	65	10	150	5	3	150	6	11	-
B-15	25	Oxalic acid	0.05	120	5	150	5	3	150	6	10	-
B-15	25	Catalyst A	0.5	65	10	150	5	3	150	6	7	-
B-15	25	$Zn(NO_3)_2$ Acetic acid	0.5 0.05	65	10	150	5	3	150	6	5	-
B-15	25	NH_4Cl	1.0	65	10	150	5	3	150	6	7	-
HA-8	25	Rhonite 401	5.0	65	10	150	5	3	150	6	60	-
HA-8	25	Catalyst A	0.5	65	10	150	5	3	150	6	45	52
HA-8	25	$Zn(NO_3)_2$ Acetic acid	0.5 0.05	65	10	150	5	3	150	6	27	-
HA-8	25	NH_4Cl	1.0	65	10	150	5	3	150	6	28	-
HA-12	25	Rhonite 401	5.0	65	10	150	5	3	150	6	57	-
HA-12	20	Catalyst A	0.5	65	10	150	5	3	150	6	33	-
HA-12	25	Catalyst A	0.5	65	10	150	5	3	150	6	71	134
HA-12	30	Catalyst A	0.5	65	10	150	5	3	150	6	51	-
HA-12	25	Catalyst A	0.5	-	-	150	3	3[d]	150	3	61	-
HA-12	25	Catalyst A	0.5	-	-	135	3	3	135	3	61	-
HA-12	25	Catalyst A	0.5	-	-	135	3	3[d]	135	3	59	-
HA-12	25	$Zn(NO_3)_2$ Acetic acid	0.5 0.05	65	10	150	5	3	150	6	27	-
HA-12	25	NH_4Cl	1.0	65	10	150	5	3	150	6	32	-

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[a] Handsheets of 50% 1.5-denier, 0.25-inch nylon and 50% wood pulp, not laminated.

[b] 200% wet pickup-treated bath concentration adjusted to give indicated solids add-on.

[c] Average of 3 measurements.

[d] 70% wet pickup, all others 100%.

a. Formula 1

A pigment combination containing Green B Paste GW-744-P, Lithosol-Fast Yellow HV Paste, and Lithosol-Red CSP Paste was recommended by K. J. Rosenlind of Kimberly-Stevens. The combination was stable in a bath with Rhoplex HA-12, but it was unstable in a dispersion with Geon 577 and antimony oxide. To avoid this stability problem, dyeing in a separate step was tried. The paper was treated first to apply 30% of Geon 577 solids and 18% of antimony trioxide and dried and cured. Then the bonded paper was padded with a dye bath that contained 3% of Green B Paste GW-744-P, 3% of Lithosol-Fast Yellow HV Paste, and 1% of Lithosol-Red CSP Paste. The wet pickup was 100%. Uneven dyeing resulted, and after the dyed paper was treated to apply 3% of FC-208, the CW resistance was unacceptable. The data in Table I-64 show the resistance of the paper to liquid VX, HD, and GB agents, as determined by the standard drop and expulsion tests. It was concluded that this method of dyeing was unsatisfactory.

b. Formula 2

A pigment composition containing 10.2% of Titanium Dispersion W-38, 54.7% of Organic Yellow Dispersion W-1840, 23.5% of Dinitraniline Organic Dispersion W-2080, and 11.7% of Carbon Black Dispersion W-7017R was next tried; but a stable dispersion with Rhoplex HA-12 could not be made. Since Formula 3 was being evaluated simultaneously and with more promise, no investigation of Formula 2 with Geon 577 was attempted.

c. Formula 3

Satisfactory dyeing of the paper was obtained with a combination of 52.63% of Multisperse Yellow M 12-961, 26.31% of Multisperse Yellow LC 12-960, and 21.06% of Multisperse Black C 11-991 in a single bath with Rhoplex HA-12. The pigments were mixed in the order listed, and the the mixture was added to the Rhoplex HA-12/Catalyst A bath in an amount equal to 10% (product basis) of the weight of the bath. A stable dispersion was obtained with which the paper could be dyed and treated with a binder simultaneously.

Table I-64. Resistance to Liquid CW Agents of Paper[a] Dyed OD

	CW Agent		
	VX	HD	GB
Drop test			
Time, hr	6	6	6
Specimens tested	3	2	1
Specimens penetrated	2	2	0
Total drops	18	12	6
Expulsion test			
Time, sec	30	30	30
Specimens tested	5	4	3
Specimens penetrated	0	0	0

---

[a] The laminated sheet for Experimental Paper No. 2-2-62 before application of binder was treated with a bath containing 25% Geon 577 solids and 15% antimony trioxide to apply 120% wet pickup. Then it was dyed, and overtreated to apply 3% FC-208 solids.

This mixture of pigments gave an unstable dispersion with the Geon 577/antimony trioxide bath, and a two-step treatment was tried. The paper was first treated with Geon 577/antimony trioxide and then dyed in a bath containing 1 part by weight of the dispersed pigments and 9 parts by weight of water. Satisfactory dyeing was also obtained in this manner.

As a result of these dyeing studies, it was decided that Formula 3 was acceptable for dyeing paper treated with either binder system.

6. Evaluation of papers treated with Rhoplex HA-12 or Geon 577/ antimony trioxide, pigments, and FC-208

Papers were treated in the laboratory according to the procedures described above for evaluation of their properties. The laminated but unbonded paper made at Kimberly-Stevens for Experimental Paper No. 2-2-62 was used for this work. The laminated paper was treated by two different methods to give: (a) a dyed paper with Rhoplex HA-12 as a binder and (b) a dyed paper with Geon 577 as a binder and antimony trioxide as a flame retardant. Both papers were overtreated with FC-208.

a. Laboratory treatment of papers

(1) Rhoplex HA-12/Catalyst A, pigments, and FC-208

The laminated base sheet of Experimental Paper 2-2-62 was treated in a bath containing 25% of Rhoplex HA-12 solids, 0.5% of Catalyst A, and 10% of Formula 3 (OD pigment combination) to apply 100% wet pickup. The paper was dried 5 minutes at 150°C, overtreated to apply 3% solids of FC-208, and then dried 5 minutes at 150°C.

(2) Geon 577, antimony trioxide, pigments, and FC-208

The laminated base sheet of Experimental Paper No. 2-2-62 was treated with a bath containing 25% of Geon 577 solids and 15% of antimony trioxide to apply 120% wet pickup and then dried 2.5 minutes at 150°C. The treated paper was dyed in a bath containing 10% of Formula 3 (OD pigment combination) to apply 100% wet pickup, dried 2.5 minutes at 150°C, overtreated to apply 3% solids of FC-208, and then dried 5 minutes at 150°C.

b. Properties of papers

(1) Physical properties

The physical properties of the two papers treated as described above are given in Table I-65, together with the physical properties of a control paper, which was similar to Experimental Paper No. 2-2-62. The control paper was prepared by treating the laminated paper used for making Experimental Paper No. 2-2-62 to apply 25% of Rhoplex B-15 solids, drying for 30 minutes at 120°C, overpadding to apply 3% FC-208 solids, and redrying for 6 minutes at 150°C.

The paper bonded with Rhoplex HA-12 had much better resistance to both wet and dry abrasion than the paper bonded with Rhoplex B-15 or Geon 577. The wet-abrasion resistance of the paper bonded with Geon 577 was somewhat less than that of the paper bonded with Rhoplex B-15, whereas the reverse was true for dry-abrasion resistance. The highest wet and dry breaking strengths were obtained with Rhoplex HA-12. Geon 577 gave a somewhat higher dry breaking strength in the machine direction of the paper than Rhoplex B-15, otherwise the breaking strengths of the papers treated with these two binders were about the same. The elongations of papers bonded with the three resins were not greatly different. The paper bonded with Rhoplex B-15 had greater tearing strengths than either of the other two papers. There were no differences of practical importance in the air permeabilities, bursting strength, or puncture strengths of the three papers. The paper bonded with Rhoplex HA-12 was slightly stiffer in the machine direction than the paper bonded with Rhoplex B-15, but the values for the stiffness of these papers in the cross direction and considerably lower in the machine direction than either of the other two papers.

(2) CW resistance

As shown by the data in Table I-66, the resistances to liquid VX, HD, and GB agents of the papers made with Rhoplex HA-12 and Geon 577, as determined by the standard drop and expulsion tests, were satisfactory. There were no penetrations of any of the specimens tested.

(3) Flame retardancy

The paper that was treated with Geon 577 and antimony trioxide, dyed, and then overtreated with FC-208 was tested for flammability. The char length of the treated paper was 7.8 inches, which was considered acceptable. Before dyeing, the char length was 5.5 inches.

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Table I-65. Properties of Reinforced Nylon-Wood Pulp Papers[a] Made in Laboratory According to Proposed Modified Procedures for Plant Production

Treatment[b]	Weight, oz/yd²		Breaking strength, lb/in.		Elongation at break, %		Elmendorf tear, g		Abrasion resistance, cycles to rupture surface layer	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg		Bursting strength, psi	Puncture strength, lb
			Machine	Cross	Machine	Cross	Machine	Cross			Machine	Cross		
Rhoplex B-15[c]	3.3	dry	21	19	22	22	2464	2688	108	43	80	91	65	4.1
		wet	16	14	26	26			90					
Rhoplex HA-12[d]	3.1	dry	27	21	20	21	851	707	225	46	99	90	61	5.0
		wet	21	17	23	24			205					
Geon 577[e] antimony trioxide[f]	3.6	dry	24	19	17	21	1344	691	144	50	63	126	54	4.3
		wet	16	13	19	23			71					

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[a] Base paper from production of Experimental Paper No. 2-2-62.

[b] All papers were overtreated to apply 3% of FC-208.

[c] Paper treated to apply 25% of B-15 solids on weight of untreated paper. Data are repeated from Table I-62.

[d] Paper treated to apply 25% of HA-12 solids, 0.5% of Catalyst A, and 10% of dispersed pigments.

[e] Paper treated to apply 30% of Geon 577 solids and 18% antimony trioxide, then treated in dye bath to apply 10% of dispersed pigments.

[f] Flame retardancy of treated paper, char length 7.8 in.

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Table I-66. Resistance to Liquid CW Agents of Dyed Papers[a] Bonded with Rhoplex HA-12 and Geon 577

Treatment	VX			HD			GB		
	Drop test[b]		Expulsion test[c]	Drop test[b]		Expulsion test[c]	Drop test[b]		Expulsion test[c]
	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated
Rhoplex HA-12, dyed OD, FC-208	0	0	0	0	0	0	0	0	0
Geon 577 Antimony trioxide Dyed OD [illegible]C-208	0[d]	0	0	0[d]	0	0	0[d]	0	0

---

[a] Base paper from production of Experimental Paper No. 2-2-62.

[b] Duration of drop test was 6 hours; one specimen was tested with 6 drops of agent; 7 to 8 mg drops.

[c] Duration of expulsion test was 1 minute; three specimens were tested, each with 1 drop of agent; 7 to 8 mg drops.

[d] Seven drops of agent per specimen.

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7. Conclusions

From the results of these studies of means of improving the propert of the reinforced nylon-wood pulp paper, the following procedures were reco mended for producing nylon-wood pulp papers with improved properties:

The base paper should be made from a 50:50 mixture of 1.5-denier, 0.25-inch nylon fibers and wood-pulp fibers. The base paper should weigh as much as possible but with the limitation that the amount of reinforced and treated paper in the overgarment must not exceed 2 pounds.

A bonded scrim of 6 x 5 strands per inch of 100-denier nylon yarn sho be laminated between two sheets of the base paper with a minimum of 24-28 of Adhesive KS-2 on the scrim and with curing conditions of at least 135°C at to 100 psi. The recommendation for the use of this scrim adhesive applied these conditions was based on laboratory data.

To obtain maximum abrasion resistance, the reinforced paper should treated to apply 25% Rhoplex HA-12 solids with 0.5% of Catalyst A, and the treated paper should be dried at 135-150°C for at least 3 minutes.

To obtain flame resistance, the reinforced paper should be treated to apply 25% of Geon 577 solids and 15% of antimony trioxide, and the treated paper should be dried at 150°C for 1.5-3.0 minutes.

For dyeing, a combination of dispersed organic pigments consisting of 52.63% Multisperse LC 12-960, 26.31% Multisperse Yellow LC-12960, and 21.06% Multisperse Black C11-991 (all on product basis) should be used. In the preparation of Rhoplex HA-12 bonded paper, 10% of the pigment mixture should be added to the Rhoplex bath, but in the preparation of the Geon 577-bonded paper, the dye must be applied in a separate step after application of the Geon. The dye bath should contain 10% of the pigment mixture (product basis), and the paper should be impregnated to apply 100% wet pickup and dri for approximately 1.5 to 3 minutes at 135-150°C.

The dyed papers should be overpadded to apply 2.5-3.0% FC-208 sol and cured at 150°C for 3-5 minutes.

The papers that are produced should be dry creped by the "Micrex" process to improve hand and flexibility.

G. Experimental Papers 6-21-62R and 6-21-62G

Two new reinforced nylon-wood pulp papers were produced during June 1962 in sufficient quantities for field evaluation. These papers were made on pilot plant scale equipment by Kimberly-Stevens Corporation at Neenah, Wisconsin, according to procedures that were developed in our laboratory. Field evaluations of the paper made previously, Experimental Paper 2-2-62, showed that it was deficient in abrasion resistance, in adhesion of the base sheets to the reinforcing scrim, and in puncture and snag resistance.

One of the new papers, 6-21-62R, was bonded with Rhoplex HA-12, an acrylic resin, which laboratory trials had indicated would provide better abrasion resistance than the bonding resin, Rhoplex B-15, used in Experimental Paper 2-2-62. An organosol of Geon 135 was used for adhering the base sheets to the scrim in this paper, and OD pigment mix was applied in combination with the Rhoplex HA-12, and the bonded laminate was aftertreated with a fluorocarbon, FC-208, to provide water and oil repellency.

The second plant-produced paper, 6-21-62G, was bonded with Geon 577, a vinyl chloride resin. Most of the Geon 577 was applied from a bath containing antimony trioxide to impart flame resistance, and the dye was applied with a small amount of the resin as a separate operation. The paper was aftertreated with FC-208 to provide water and oil repellency. Although it was not expected that this fabric would be as resistant to abrasion as the fabric bonded with Rhoplex HA-12, it was made to provide a flame resistant paper for evaluation. No practical method is known for imparting flame resistance to papers bonded with acrylic resins.

Both of the new plant-produced papers showed the expected improvements in physical properties, relative to Experimental Paper 2-2-62, in laboratory evaluations. Creping was effective for improving the flexibility of the papers without reducing the CW resistance below acceptable limits.

1. Plant production of Experimental Papers 6-21-62R and 6-21-62G

a. Preparation of reinforced paper laminate

Thirty-eight hundred yards of 0.9 oz/yd^2 base sheet containing 50% of 1.5-denier, 0.25-inch nylon and 50% of Hermac kraft was made on a Fourdrinier machine; and a scrim containing 6 x 5 strands per inch of 100-denier, high-tenacity nylon was laminated between two layers of the base sheet. The warp and filling yarns of the scrim were bonded together by applying polyvinyl acetate (AYAT or equivalent in Solox or acetone) to the warp yarns. The bonded scrim was coated with 27.0 to 29.5 g/yd^2 of an organosol (85% Geon 135 in dioctyl phthalate and 15% mineral spirits) and immediately sandwiched between the base sheets. The laminate was then dried and hot calendered twice. The weight of the laminated paper was 3.02 to 3.16 oz/yd^2. The conditions for preparing the laminated paper are shown in Table I-67.

b. Treatment of reinforced paper laminate

Approximately one-half of the laminated paper produced was treated with a combination of Rhoplex HA-12 bath and an OD pigment mix, dried, and then aftertreated with FC-208. This paper was designated Experimental Paper 6-21-62R. The other half of the paper was treated with a combination of Geon 577 and antimony trioxide, dried, treated with a combination of Geon 577 and OD pigment mix, again dried, and then aftertreated with FC-208. This paper was designated Experimental Paper 6-21-62G.

The formulations for the treating baths are given in Table I-68. The plant conditions for the treatments and the solids add-ons obtained are given in Table I-69. During the impregnation of 6-21-62R, there was a slight build-up of Rhoplex HA-12 on the bottom impregnation roll, and there was some build-up on the edge of the first few drying rolls. During the dyeing of 6-21-62G, there was considerable build-up of Geon 577 and dye pigments of the drying cans.

The final weight of Experimental Paper 6-21-62R was 3.86 oz/yd^2, and the final weight of Experimental Paper 6-21-62G was 4.42 oz/yd^2.

Table I-67. Plant Conditions for Laminating Base Paper

Speed, ft/min	325-330
Temperature of drying rolls (3), °C	182
Temperature of calender, °C	132
Pressure of calender,	
gauge	550
lb per inch of roll length	228

Table I-68. Treating Baths for Experimental Papers 6-21-62R and 6-21-6

	Weight, lb	% in bath product basis	% in bath solids basis
A. Rhoplex HA-12/OD dye bath[a]			
Rhoplex HA-12[b]	389.0	55.4	25.5
Multi-Sperse Yellow M 12-961	36.84	5.3	2.2
Multi-Sperse Yellow L 12-960	18.42	2.6	1.0
Multi-Sperse Black C 11-991	14.78	2.1	0.9
Catalyst A	3.50	0.5	0.5
Water	237.6		
B. Geon 577-antimony trioxide bath[b]			
Geon 577	288	36.0	20.0
Antimony trioxide dispersion	260	32.5	13.0
Water	252	-	-
C. Geon 577/OD dye bath			
Geon 577	36.5	4.87	2.67
Multi-Sperse Yellow M 12-961	53.5	7.13	2.92
Multi-Sperse Yellow L 12-960	26.8	3.57	1.49
Multi-Sperse Black C 11-991	21.5	2.87	1.02
Water	611.7		
D. FC-208 bath			
FC-208	135	20.0	5.6
Water	542		

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[a] 150 cc of 2-ethyl-1-hexanol added.

[b] 250 cc of 2-ethyl-1-hexanol added.

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Table I-69. Plant Conditions for Applying Treatments to Experimental Papers 2-21-62R and 2-21-62G

Conditions	2-21-62R		2-21-62G		
Treating bath (solids basis)	25% HA-12 3.9% OD dye	5.6% FC-208	20% Geon 577 13% antimony trioxide	2.67% Geon 577 6.14% OD dye	5.6% FC-208
Squeeze roll pressure, psi gauge	15	5	15	5	10
Wet pick-up, %	97.5	47	101	61	50-55
Solids add-on, %	24.9 Rhoplex HA-12 4.0 OD dye	2.5	20.2 Geon 577 13.1 antimony trioxide	1.63 Geon 577 3.31 OD dye	2.8-3.1
Temperature of drying rolls, °C	149-154	149-154	149-154	149-154	149-154
Time of drying, min	1.5[a]	1.5[a]	1.5	1.3	1.5[a]
Speed, ft/min	150	150	150	175	150

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[a] Material was redried under the same conditions of temperature and speed.

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2. Effects of Creping on Properties of the Papers

Experimental Paper 6-21-62R bonded with Rhoplex HA-12 was creped 8.3, 14.6, and 30%. Experimental Paper 6-21-62G bonded with Geon 577, was creped 6.3, 10.9, 16.7, and 30%. The percentage of crepe = 100 x (uncreped length - creped length)/uncreped length. A portion of each of the creped papers was drawn to approximately its original length. After release of the tension applied to draw the creped papers, some contraction took place, but the amount was not determined. Drawing after creping did not appear to reduce the benefits of creping on either the hand or the flexibility of a paper.

The physical properties that were measured are given in Table I-70, and data on the resistance of the papers to CW agents are given in Table I-71.

a. Physical properties

Creping and drawing did not appreciably affect the weight per square yard of 6-21-62R, but the weight of 6-21-62G was increased by these treatments. The breaking strengths and elongations at break of the papers were not significantly changed by creping and drawing.

Erratic changes in machine tearing strength (paper torn across the machine direction) occurred when 6-21-62R was creped. The machine tearing strength of 6-21-62G was decreased by creping. The cross tearing strengths of both 6-21-62R and 6-21-62G were decreased markedly by creping. In general, the tearing strength of the creped and drawn papers were not greatly different than the tearing strengths of the corresponding creped and undrawn papers.

The dry and wet abrasion resistance of the creped papers were generally greater than those of the corresponding uncreped papers. This increase in abrasion resistance was probably caused by the increased thickness of certain areas of the papers resulting from the creping operation. There appeared to be no correlation between the percentage of creping and the abrasion resistance of the creped papers. The abrasion resistances of creped and drawn papers were not greatly different from those of the corresponding creped and undrawn papers.

Table I-70. Physical Properties of Creped and Uncreped Plant-Produced Experimental Papers 6-21-62 R and 6-21-62 G

Description	Weight, oz/yd²	Creped,[a] %		Breaking strength, lb/in.		Elongation at break, %		Elmendorf tear, g		Abrasion resistance, cycles to rupture	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg		Bursting strength, psi	Puncture strength, lb	Peel strength, lb/in.	
				Machine	Cross	Machine	Cross	Machine	Cross			Machine	Cross			Machine	Cross
A. Uncreped Papers																	
2-2-62[b]	3.2	0	dry	25	19	14	20	2237	1872	108	32	53	32	59	3.9	0.5	0.8
			wet	18	14	17	20			90							
6-21-62 R	3.9	0	dry	31	18	20	26	1190	1190	356	16	113	119	67	4.9	2.3	1.8
			wet	25	14	23	26			207							
6-21-62 G	4.4	0	dry	31	20	18	24	2067	1408	228	16	135	135	63	5.9	2.3	1.9
			wet	21	12	23	24			101							
B. Creped Papers																	
6-21-62 R	4.2	8.3 UD	dry	26	22	24	23	1329	467	602	6	76	104	73	6.4	-	-
			wet	25	15	28	24			412							
6-21-62 R	4.0	8.3 D	dry	36	22	24	25	842	451	454	6	77	114	75	6.0	-	-
			wet	24	14	27	21			349							
6-21-62 R	4.1	14.6 D	dry	36	21	26	23	1114	474	515	7	75	96	73	5.9	-	-
			wet	25	16	28	23			548							
6-21-62 R	3.8	30 D	dry	29	18	21	25	1323	416	730	13	47	63	68	5.2	2.3	1.9
			wet	21	13	25	25			543							
6-21-62 G	4.8	6.3 D	dry	30	20	19	26	1568	698	388	16	72	102	62	5.5	-	-
			wet	22	13	24	24			207							
6-21-62 G	4.8	10.9 UD	dry	27	19	18	25	1651	570	323	13	55	110	63	5.7	-	-
			wet	19	13	22	25			213							
6-21-62 G	4.7	10.9 D	dry	29	19	19	26	1277	643	247	12	52	92	68	5.9	-	-
			wet	20	11	24	24			133							
6-21-62 G	5.0	16.7 UD	dry	28	16	21	18	1709	531	252	13	63	109	63	5.2	-	-
			wet	23	13	23	24			193							
6-21-62 G	4.9	16.7 D	dry	28	19	21	25	1594	563	319	13	64	108	63	4.6	-	-
			wet	19	11	20	23			174							
6-21-62 G	4.5	30 D	dry	27	17	20	24	1554	654	214	14	53	76	62	5.0	2.4	1.8
			wet	18	12	22	23			164							

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[a] UD - undrawn, D - drawn.

[b] Data from Table I-54.

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Table I-71. Resistance to Liquid CW Agents of Creped and Uncreped Plant-Produced Experimental Papers 6-21-62 R and 6-21-62 G[a]

Paper	Creped, %[b]	VX Drop test Specimens penetrated	VX Drop test Drops penetrated	VX Expulsion test Specimens penetrated	HD Drop test Specimens penetrated	HD Drop test Drops penetrated	HD Expulsion test Specimens penetrated	GB Drop test Specimens penetrated	GB Drop test Drops penetrated	GB Expulsion test Specimens penetrated
6-21-62 R	0	0/4	0/24	0/10	0/4	0/24	0/10	0/4	0/24	0/10
	8.3 D	0/2	0/6	0/10	0/2	0/6	0/10	0/2	0/6	0/10
	14.6 UD	1/1	1/6	0/10	1/1	1/6	0/10	1/1	1/6	0/10
	14.6 D	0/1	0/6	0/10	0/1	0/6	0/10	1/1	1/6	0/10
	30 D	3/3	9/18	2/9	3/3	12/18	0/9	1/3	2/18	0/9
6-21-62G	0	0/4	0/24	0/10	1/4	1/24	0/10	0/4	0/24	0/10
	6.3 D	0/2	0/6	0/10	0/2	0/6	0/10	0/2	0/6	0/10
	10.9 UD	0/1	0/6	0/10	-	-	-	-	-	-
	10.9 D	0/2	0/6	0/10	0/2	0/6	0/10	0/2	0/6	0/10
	16.7 D	0/2	0/6	0/10	1/2	1/6	0/10	0/2	0/6	0/10
	30 D	1/3	1/18	0/9	3/3	6/18	1/9	1/3	1/18	0/9

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[a] Specimens or drops penetrated/specimens or drops tested; 7 to 8 mg drops.

[b] UD = undrawn, D = drawn.

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The air permeability of 6-21-62R was reduced by all of the creping treatments, but not to below an acceptable level. The air permeability of 6-21-62G was reduced only very slightly by the treatments.

The stiffness of the papers was decreased by creping. The decrease was greater in the machine direction than in the cross direction, as would be expected. The measured decrease in stiffness agrees with the observed improvement in hand produced by creping.

No significant differences were observed in the bursting and puncture strenghts of the uncreped papers and the corresponding creped papers.

The peel strengths of 6-21-62R and 6-21-62G creped 30% were the same as those of the corresponding uncreped papers; so the peel strengths of papers creped less than 30% were not determined.

b. Resistance to liquid CW agents

Table I-71 shows the resistances to liquid VX, HD, and GB agents of the uncreped and creped Experimental Papers 6-21-62R and 6-21-62G.

Experimental Paper 6-21-62R uncreped or creped 8.3% and drawn was resistant to the three liquid CW agents by the standard drop and expulsion tests. When it was creped 14.6% and not drawn, it was penetrated by all three agents; but, when it was creped 14.6% and drawn, it was penetrated only by GB agent. All three CW agents penetrated 6-21-62R when it was creped 30% and drawn.

Experimental Paper 6-21-62G uncreped, creped 6.3% and drawn, or creped 10.9% and drawn was resistant to all three liquid CW agents. Uncreped paper 6-21-62G was penetrated by 1 drop out of 24 drops of HD agent, but this was attributed to a flaw in the paper. Paper 6-21-62G that was creped 16.7% and drawn was penetrated by HD agent, but was resistant to VX and GB agents. Paper 6-21-62G that was creped 30% and drawn was penetrated by all three CW agents.

3. Properties of papers used in the field evaluation

The papers that were selected for field evaluation were uncreped Experimental Paper 6-21-62R* and Experimental Paper 6-21-62G* that had been creped 10.9% and drawn. The latter paper was designated 6-21-62GCD. The choice of these papers was based on hand and flexibility, physical properties, CW resistance, and flame retardancy.

Uncreped paper 6-21-62R was chosen to provide a direct comparison with Experimental Paper 2-2-62, which was previously field evaluated, and thus to provide a comparison of the effects of Rhoplex HA-12 and Rhoplex B-15 on the paper properties. Experimental Paper 6-21-62GCD was selected for field evaluation because of the flame resistance of the paper, and creping was necessary to increase its flexibility.

Table I-72 shows the physical properties of the two papers that were selected for field evaluation along with those of Experimental Paper 2-2-62 that was evaluated in the previous field trials.

The weights of papers 6-21-62R and 6-21-62 GCD were greater than the weight of paper 2-2-62 (3.9 and 4.7 vs 3.2 oz/yd^2, respectively), as a result of greater amounts of scrim adhesive in both 6-21-62R and 6-21-62GCD and the weight of the flame retardant in 6-21-62GCD. The weight of 6-21-62 GCD was also increased as a result of the creping operation.

The breaking strengths of papers 6-21-62R and 6-21-62GCD in the machine direction were higher than the corresponding breaking strength of paper 2-2-62. All three papers had approximately the same breaking strengths in the cross direction.

The elongations at break were generally less in the machine direction than in the cross direction. The elongations at break of papers 6-21-62R and 6-21-62GCD were greater than those of paper 2-2-62.

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* Samples of these papers are included in the Appendix.

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Table I-72. Physical Properties of Reinforced Nylon-Wood Pulp Papers for Field Evaluation

Description	Weight, oz/yd^2	Creped,[a] %		Breaking strength, lb/in.		Elongation at break, %		Elmendorf tear, g		Abrasion resistance, cycles to rupture	Air permeability, ft^3/min/ft^2, 0.5 in. water	Stiffness, mg		Bursting strength, psi	Puncture strength, lb	Peel strength, lb/in.	
				Machine	Cross	Machine	Cross	Machine	Cross			Machine	Cross			Machine	Cross
2-2-62[b]	3.2	0	dry	25	19	14	20	2237	1872	108	32	53	32	59	3.9	0.5	0.8
			wet	18	14	17	20			90							
6-21-62 R	3.9	0	dry	31	18	20	26	1190	1190	356	16	113	119	67	4.9	2.3	1.8
			wet	25	14	23	26			207							
6-21-62GCD	4.7	10.9	dry	29	19	19	26	1277	643	247	12	55	110	68	5.9	2.3	1.9
			wet	20	11	24	24			133							

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[a] Creped and then drawn to approximately the original length.

[b] Data from Table I-54.

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The machine tearing strengths (paper torn across the machine direction) of papers 6-21-62R and 6-21-62GCD were approximately the same, but both were lower than the corresponding tearing strength of paper 2-2-62. The cross tearing strength of paper 2-2-62 was greater than the corresponding tearing strengths of paper 6-21-62R and 6-21-62GCD (1872 vs 1190 and 643, respectively).

The wet abrasion resistance of paper 6-21-62R was 1.5 times that of paper 6-21-62GCD and twice that of paper 2-2-62. The dry abrasion resistance values were in the same order. (Values obtained by U. S. Army Natick Laboratories by a method involving rubbing the papers over wet sand showed that the wet abrasion resistances of the papers were in the order 6-21-62R (best), and uncreped 6-21-62G.)

Papers 6-21-62R and 6-21-62GCD had acceptable air permeabilities, but the values were half (or less) the value for paper 2-2-62.

The stiffness values for papers 2-2-62 and 6-21-62GCD were the same and were about half that for paper 6-21-62R in the machine direction. In the cross direction, the stiffness values of papers 6-21-62R and 6-21-62GCD were the same and were about 3 times the value of paper 2-2-62.

No significant differences were observed for the bursting and puncture strengths of the three papers.

Papers 6-21-62R and 6-21-62GCD had much higher peel strengths (scrim to paper adhesion) than paper 2-2-62.

4. Field evaluation of Experimental Papers 6-21-62R and 6-21-62GCD

Overgarments were made from Experimental Paper 6-21-62R and 6-21-62GCD by International Latex Corporation and submitted to the U. S. Army Natick Laboratories for field evaluation. The overgarments were evaluated at Fort Lee, Virginia, during November and December, 1962 on the Cotton Fabric Course.

The results of these trials were reported in detail by the U. S. Army Research and Engineering Field Agency; hence, only a summary of the findings is given here.

- There was no significant difference between the durability of Experimental Paper 6-21-62R and Experimental Paper 6-21-62GCD.

- There was no different in frequency of holes, tears, and wear areas for the two papers.

- Both papers were estimated to have a service life of 3-4 days.

H. Experimental Nonwoven Fabrics

Nonwoven fabrics and laminates of a lightweight woven nylon fabric with nonwoven fabrics were investigated in an effort to find base materials for the overgarment that had physical properties superior to the experimental papers. Nonwoven fabrics made from nylon, rayon, or mixtures of rayon and nylon were prepared for us by J. P. Stevens and Company. The compositions, weights, and designations of the fabrics are given in Table I-73.

1. Screening studies

For preliminary evaluation of the nonwoven fabrics Fabric No. 1 and Fabric No. 3 were treated with Rhoplex B-15, an acrylic resin, and the properties of the treated fabrics were determined with results as given in Table I-74.

Samples of the two fabrics (1 and 3) were padded with baths containing Rhoplex B-15, Rhonite 401, and Catalyst AC in the ratio of 20:4:1 (solids) to apply 20, 40, and 60% total solids. The padded samples were dried 10 minutes at 65°C and cured 10 minutes at 150°C. The total resin contents based on fiber plus resin were approximately 33%, 43%, and 50%. The later amounts include the resin applied in production of the fabrics by J. P. Stevens (Table I-74).

In general, the breaking strengths, elongations at break, abrasion resistance, bursting and puncture strengths, and stiffness of the fabrics increased as the binder content was increased; whereas the tearing strengths and air permeabilities decreased. With the same amount of binder, Fabric No. 3 had greater dry breaking strength, machine tearing strength, air permeability, bursting strength and puncture strength than Fabric No. 1, and less elongation at break and cross tearing strength.

Samples of the treated nonwoven Fabrics No. 1 and No. 3 containing 33% of Rhoplex B-15 solids were treated to apply 3% FC-208, and evaluated for resistance to liquid VX agent. The samples were not penetrated by the liquid VX agent in the standard drop or expulsion tests.

Table I-73. Compositions of Nonwoven Fabrics

Fabric	Weight, oz/yd²	Composition[a]
1	3.0	40% 1.5-denier, 2.5-inch nylon; T-201, semi-dull 40% 1.5-denier, 2-inch rayon; Narcon No. 2, bright 20% Rhoplex B-15
3	3.0	40% 2.3-denier, 2-inch nylon; T-420, semi-dull 40% 1.5-denier, 2-inch rayon; Narcon No. 2, bright 20% Rhoplex B-15
5	2.0	47.5% 1.5-denier, 2.5-inch nylon; T-201, semi-dull 47.5% 1.5-denier, 2-inch rayon; Narcon No. 2, bright 5.0% Rhoplex B-15
7	2.0	95% 1.5-denier, 2-inch rayon; Narcon No. 2, bright 5% Rhoplex B-15
9	2.2	88.5% 1.5-denier, 2.5-inch nylon; T-201, semi-dull 11.5% Rhoplex B-15

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[a] T - 201 is normal tenacity, heat-set nylon
T - 402 is high tenacity, no-crimp nylon
Narcon No. 2 is a high-tenacity rayon
Rhoplex B-15 is an acrylic binder

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Table I-74. Physical Properties of Nonwoven Fabrics Treated to Contain Various Amounts of Binder[a]

Fabric	Composition of fabrics, % Fiber	Composition of fabrics, % Resin	Weight, oz/yd²		Breaking strength, lb/in. Machine	Breaking strength, lb/in. Cross	Elongation at break, % Machine	Elongation at break, % Cross	Elmendorf tear, g Machine	Elmendorf tear, g Cross	Abrasion resistance, cycles to rupture	Air permeability, ft³/min/ft², 0.5 in. water	Stiffness, mg Machine	Stiffness, mg Cross	Bursting strength, psi	Puncture strength, lb
1	67	33	3.3	dry	19	19	27	37	1459	1411	525	165	96	99	84	11.3
				wet	14	12	29	33								
1	57	43	3.9	dry	28	24	30	39	931	822	680	160	160	126	100	12.6
				wet	19	15	33	39								
1	50	50	4.7	dry	34	29	37	42	666	550	1104	130	201	129	109	12.2
				wet	23	19	35	39								
3	67	33	3.1	dry	23	18	21	25	1939	1469	260	215	164	132	120	12.8
				wet	12	10	20	25								
3	57	43	3.6	dry	31	26	24	28	1165	1037	357	185	186	158	>120	16.6
				wet	19	17	24	33								
3	50	50	4.8	dry	41	38	28	32	749	525	1478	140	254	237	>120	17.3
				wet	28	21	27	31								

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[a] Fabrics containing 20% Rhoplex B-15 solids were treated from baths containing Rhoplex B-15, Rhonite 401, and Catalyst AC in the ratio of 20:4:1 to apply 20, 40, and 60% solids. Treated samples were dried 10 minutes at 66°C and cured 10 minutes at 149°C.

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2. Effects of variables on properties

The screening studies just described indicated that it might be possible to make a nonwoven fabric that would meet most of the requirements for the overgarment material. Therefore, studies were made to determine the type of fiber type, the type of binder, and the fiber/binder ratio that would produce a nonwoven fabric with optimum physical properties.

a. Treatments

Samples of the five nonwoven fabrics described above (No. 1, 3, 5, 7, and 9) were padded with baths containing: (1) Rhoplex B-15, Rhonite 401, and Catalyst A in the ratio of 20:4:1 (solids), and (2) Rhoplex HA-12 with Catalyst A (0.5% of the bath) to apply approximately 20, 30, and 40% total solids based on the fabrics as received. Samples of Fabrics No. 1 and No. 3 were also padded with a bath containing 20% Geon 577 and 13% antimony trioxide to apply approximately 33% solids to the fabrics as received. The padded samples were dried 10 minutes at 66°C. Samples of each of the treated and dried fabrics were cured in two ways: (1) in an oven for 10 minutes at 150°C and (2) in a hydraulic press for 5 minutes at 150°C and 100 psi. All samples were aftertreated to apply 3% FC-208 solids, dried, and cured 6 minutes at 150°C.

b. Properties

The air permeability and resistance to liquid VX agent of each of the treated fabrics are given in Table I-75.

The air permeabilities of all of these treated nonwoven fabrics were well above the minimum value considered acceptable at the time of the investigation (6 $ft^3/min/ft^2$); although the values for the fabrics cured in a press were appreciably lower than for the fabrics cured in an oven, as would be expected. Increased resin content also decreased the air permeability of each fabric.

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Table I-75. Properties of Nonwoven Fabrics Treated with Different Binders[a]

Fabric	Composition of fabric, % Fiber	Composition of fabric, % Resin[b]	Resistance to VX agent[c] Oven cure	Resistance to VX agent[c] Press cure	Air permeability, ft³/min/ft², 0.5 in. water Oven cure	Air permeability, ft³/min/ft², 0.5 in. water Press cure	Breaking strength,[d] lb/in.	Elongation at break, %[d]	Elmendorf tear, g[d]	Wet abrasion resistance, cycles to rupture
A. Rhoplex B-15[e]										
1	67	33	0	5	170	60	22	25	1472	267
3	67	33	0	5	180	65	26	19	1994	254
5	79	21	2	7	165	55	19	25	1493	103
7	79	21	1	7	105	49	24	24	970	96
9	74	26	0	8	250	78	14	32	2410	150
1	62	38	1	8	140	45				
3	62	38	1	7	145	45				
5	73	27	3	8	150	58				
7	73	27	4	7	95	35				
9	68	32	3	8	205	49				
1	57	43	0	6	120	31				
3	57	43	0	6	150	25				
5	68	32	0	7	143	23				
7	68	32	6	8	80	25				
9	63	37	0	8	175	47				
B. Rhoplex HA-12[f]										
1	67	33	0	8	125	44	20	22	1664	283
3	67	33	0	8	145	60		16	1856	254
5	79	21	4	8	155	80	19	25	1792	153
7	79	21	2	8	98	45	18	17	1863	102
9	74	26	0	8	210	75	23	36	2888	288
1	62	38	0	8	115	36				
3	62	38	0	8	135	40				
5	73	27	6	8	130	60				
7	73	27	3	8	95	40				
9	68	32	2	7	185	60				
1	57	43	0	7	85	24				
3	57	43	0	8	95	27				
5	68	32	2	8	100	30				
7	68	32	2	8	65	30				
9	63	37	2	8	135	34				
C. Geon 577-Sb_2O_3[g]										
1	60	30	0	5	140	78	17	20	2080	
3	60	30	-	1	190	85	21	17	2762	

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[a] Aftertreated to apply 3% FC-208 solids.

[b] Resin in fabric when received plus resin applied as aftertreatment.

[c] Drops penetrated of 8 drops used in expulsion test, 7 to 8 mg drops.

[d] Machine direction.

[e] Fabrics as received treated with baths containing Rhoplex B-15, Rhonite 401, and Catalyst AC in the ratio of [illegible] to apply [illegible], [illegible], and [illegible] solids.

[f] Fabrics as received treated with baths containing Rhoplex HA-12 and Catalyst A ([illegible] of bath) to apply [illegible], [illegible], and [illegible] solids.

[g] Fabrics as received treated with baths containing [illegible] Geon 577 and [illegible] to apply [illegible]

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The expulsion test was used to determine the resistance of the treated fabrics to liquid VX agent. All of the treated fabrics that were cured in a press had unacceptable resistance to liquid VX agent (5 out of 8 drops penetrated). The only oven-cured fabrics that had generally acceptable resistance to liquid VX agent, regardless of the binder used, were Fabrics No. 1 and No. 3.

The data on the physical properties of the nonwoven fabrics treated with 20% binder and then oven cured showed that: (1) the treated 3 oz/yd^2 Fabrics (1 and 3) provided more resistance to abrasion and VX agent than the correspondingly treated 2 oz/yd^2 Fabric (5, 7, and 9), (2) the treated fabric should be oven cured rather than press cured, and (3) the treated nylon Fabric (9) had greater tearing strength, abrasion resistance, and resistance to VX agent than the comparable treated rayon Fabric (7). It was felt that the advantages gained by the use of nylon might be offset by the possible difficulty in flameproofing nylon nonwoven fabrics and thus work was continued with the all-rayon nonwoven fabric as well as the all-nylon nonwoven fabric.

3. Investigation of other binders

Additional binders were investigated in attempts to produce nonwoven fabrics having good physical properties for the overgarments and also good flame retardant properties. Nylon webs and rayon webs (without binder) were treated with Thiokol WD-6, a polysulfide rubber; with Parlon S-20, a chlorinated rubber; with Lexan 125, a polycarbonate resin; with Multranil 176, a polyurethane resin; with Elastothane 455, a polyurethane rubber; and with Rhoplex HA-12, an acrylic resin. The fabrics treated with Rhoplex HA-12 were used as controls since previous results had shown that, in general, fabrics containing Rhoplex HA-12 as binder had good overall properties for use in overgarments.

a. Treatments

Samples of a 1.9 oz/yd^2 nylon web (1.5-denier, 2.5-inch, semi-dull, normal tenacity fibers) and of a 1.9 oz/yd^2 rayon web (1.5-denier, 2-inch, bright, high tenacity fibers) were treated as follows:

by padding with each of the following baths: (a) 20% Thiokol WD-6 solids in water, (b) 15% Parlon S-20 solids in toluene, and (c) 20% Rhoplex HA-12 solids in water (with 0.5% Catalyst A based on the bath weight); and

by immersing in each of the following baths: (a) 2.5% Lexan 125 solids in tetrachloroethane, (b) 7% Multranil 176, 2.3% Mondur CB-75 solids (curing agent), and 1.2% Catalyst CE solids in ethyl acetate, and (c) 5% Elastothane 455 solids in 2-butanone.

The samples padded with Rhoplex HA-12 were dried 10 minutes at 66°C and the other treated samples were air dried. The samples treated with Thiokol WD-6 and Parlon S-20 were cured at room temperature, those treated with Lexan 125 were cured 3 minutes at 160°C, those treated with Multranil 176 were cured 5 minutes at 110°C, and those treated with Elastothane 455 were cured 45 minutes at 140°C.

The fiber to binder ratios of the treated fabrics was about 60:40 or 65:35, and the weights of the treated fabrics ranged from 2.4 to 3.5 oz/yd^2.

b. Properties

(1) Physical properties

As shown in Table I-76, the nylon and rayon webs treated with Rhoplex HA-12 both had good properties except for stiffness. Both the nylon and the rayon nonwoven fabrics treated with Rhoplex HA-12 had higher breaking strengths, abrasion resistance, and bursting strengths, than the other treated fabrics, but the tearing strengths were lower. Multranil 176 was the next best binder. Compared to fabrics treated with Rhoplex HA-12, fabrics treated with Multranil 176 had much lower breaking strengths and abrasion resistance, but they had higher tearing strengths and about the same bursting strengths.

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Table I-76 Properties of Nylon and Rayon Nonwoven Fabrics Treated with Various Binders

Fabric	Binder	Composition of fabric, % Fiber	Composition of fabric, % Binder	Weight, oz/yd²	Breaking strength,[a] lb/in.	Elongation at break,[a] %	Elmendorf tear,[a] g	Abrasion resistance, cycles to rupture	Air permeability, ft³/min/ft², 0.5 in. water	Bursting strength, psi	Handle
Nylon	Rhoplex HA-12	65	35	3.4	33	44	1075	1341	223	99	stiff
Nylon	Thiokol WD-6	65	35	3.0	13	52	2976	281	230	73	stiff
Nylon	Parlon S-20	69	31	2.8	4	17	1779	85	387	52	pliable
Nylon	Lexan 125	77	23	2.5	6	29	2048	132	347	68	stiff
Nylon	Multranil 176	60	40	3.4	15	43	2818	404	200	33	pliable
Nylon	Elastothane 455	63	37	3.0	7	31	2272	238	395	60	pliable
Rayon	Rhoplex HA-12	66	34	3.1	30	20	1056	928	105	93	stiff
Rayon	Thiokol WD-6	65	35	3.3	20	30	1530	74	98	85	stiff
Rayon	Parlon S-20	69	31	2.4	5	7	1344	24	408	39	pliable
Rayon	Lexan 125	80	20	2.8	9	19	1632	118	320	55	stiff
Rayon	Multranil 176	62	38	3.5	19	18	1408	222	135	92	stiff
Rayon	Elastothane 455	65	35	3.4	12	17	1760	71	280	86	stiff

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[a] Machine direction.

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The nonwoven fabrics treated with the other binders generally had exceptionally low breaking strengths and abrasion resistance, even though they all had high tearing strengths and some of them had high bursting strengths. All of the fabrics had high air permeabilities, but many of the fabrics were stiff. Only the nylon fabrics treated with Parlon S-20, Multranil 176, and Elastothane 455 and the rayon fabric treated with Parlon S-20 were pliable.

It had been expected that the use of polyurethane binders (Multranil 176 and Elastothane 455) would provide fabrics with outstanding resistance to abrasion, but the data showed that the abrasion resistances of fabrics treated with either Multranil 176 or with Elastothane 455 were quite low. An investigation of different curing conditions for the polyurethane binders showed that the abrasion resistance of the polyurethane-treated fabrics could be increased above the values given in Table I-76; however, the values were still considerably below the abrasion resistance of the corresp fabric treated with Rhoplex HA-12.

(2) Flame resistance

The flame resistance of each of the treated nonwoven fabrics was estimated by the match test. All of the fabrics were consumed, but those containing Rhoplex HA-12 burned more slowly than the fabrics containing the other binders. The more rapid burning of the fabrics treated with Parlon S-20 was surprising since it was expected that the chlorine content (approximately 65%) of the Parlon S-20 would increase the flame resistance of the treated fabrics. However, the more open and loosely bonded structur of the Parlon-bonded fabrics probably increased the combustibility of the fabric so that the flame retardant effect of the Parlon S-20 was minimized.

4. Nonwoven fabric/fabric laminates

Laminates were prepared from nonwoven fabrics and a lightweight nylon fabric in an attempt to prepare a material with properties superior to those obtained with only a nonwoven fabric treated with a binder.

a. Treatments

Laminates were prepared from Fabrics 1, 3, 5, 7, and 9, and a 1.1 oz/yd^2 nylon parachute fabric. A combination of Rhoplex B-15, Rhonite 401, and Catalyst AC (20:4:1 solids ratio) and a combination of Rhoplex HA-12 and Catalyst A (0.5% of the bath) were tried as binders.

The laminates were treated to apply 20, 30, and 40% solids of the binders. After treatment, the laminates were dried 10 minutes at 66°C and then cured in two different ways: (1) in an oven for 10 minutes at 150°C and (2) in a hydraulic press for 5 minutes at 150°C and 100 psi. The laminates were aftertreated to apply 3% of FC-208 solids and then dried and cured 6 minutes at 150°C.

b. Properties

As shown in Table I-77 the air permeabilities of all of the laminates that were oven-cured were acceptable (>6 ft^3/min/ft^2). Of the samples that were cured in a press, all samples that were treated to apply 20 or 30% solids of either resin combination had acceptable air permeabilities, but those treated to apply 40% solids had permeabilities that were either below the acceptable value or only slightly above.

The resistance to VX agent of the laminates treated to apply 20% solids were determined by the expulsion test and the results are given in Table I-77. The resistance to liquid VX of the laminates that were oven cured were generally acceptable, but those of the laminates that were press cured were all unacceptable.

The peel strengths of all of the laminates that were cured in the oven were unacceptably low; the laminates cured in the press had acceptable peel strengths. Since the laminates with acceptable peel strengths were not resistant to liquid VX agent, no further work was done on this type of laminate.

Table I-77. Properties of Woven Nylon Fabric/Nonwoven Fabric Laminates Treated with Rhoplex B-15 and with Rhoplex HA-12[a]

Nonwoven fabric in laminate[b]	% Add-on	CW resistance[c]		Air permeability, $ft^3/min/ft^2$, 0.5 in. water	
		Oven cure	Press cure	Oven cure	Press cure
A. Rhoplex B-15					
1	20	0	7	38	11
3	20	0	7	48	16
5	20	0	8	46	20
7	20	0	4	42	14
9	20	1	7	60	17
1	30			33	10
3	30			38	12
5	30			41	11
7	30			35	9
9	30			42	10
1	40			27	5
3	40			32	5
5	40			25	5
7	40			32	8
9	40			28	5
B. Rhoplex HA-12					
1	20	1	5	40	18
3	20	0	8	41	22
5	20	0	7	40	21
7	20	0	4	39	16
9	20	0	6	51	23
1	30			33	6
3	30			34	9
5	30			31	15
7	30			35	12
9	30			34	10
1	40			29	6
3	40			37	10
5	40			27	7
7	40			29	7
9	40			24	3

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[a] Aftertreated to apply 3% FC-208 solids.

[b] Each nonwoven fabric laminated to woven nylon fabric.

[c] Drops penetrated of 8 drops used in VX expulsion test, 7 to 8 mg drops.

1. Pilot-Plant Production of Nonwoven Fabrics

Two nonwoven fabrics were made according to our recommendations by J. P. Stevens and Company. One of the nonwoven fabrics was made from nylon fibers because our previous studies showed that all-nylon nonwoven fabrics had greater tearing strength and abrasion resistance than nonwoven fabrics made from either rayon or blends of rayon and nylon. The nylon nonwoven fabric, designated Experimental Nonwoven Fabric 10-30-62 N, was treated with a plasticized Geon 351, Apex Flameproof 290 B, and FC-208 to produce a flame-retardant, CW-resistant material.

Due to the known difficulty of flameproofing nylon nonwoven fabrics, a nonwoven fabric was also made from rayon fibers. The rayon nonwoven fabric, designated Experimental Nonwoven Fabric 10-30-62 R, was treated with a 1:1 solids ratio of Rhoplex HA-12 and Rhoplex HA-8, because our previous work on papers had shown that Rhoplex HA-12 alone gave a very stiff material, and it was hoped that by the use of a mixture of these acrylic binders that the good wet abrasion obtained from Rhoplex HA-12 could be maintained and that the Rhoplex HA-8 would decrease the stiffness. The rayon nonwoven was treated with Apex Flameproof 290 B to make it flame retardant and with FC-208 to impart CW resistance.

Both of the experimental nonwoven fabrics had generally better physical properties than the most promising reinforced paper made previously (6-21-62 R) but they were stiffer and heavier. The nylon fabric was reasonably flame resistant, but the flame resistance of the rayon fabric varied from spot to spot indicating uneven treatment. Conversely, the rayon fabric showed generally good resistance to liquid CW agents, but the nylon fabric was not uniform in this respect. The non-uniformity could probably be overcome by modification of processing conditions, but further plant rrials did not appear warranted.

1. Methods of preparation

From the results of our earlier studies and some suggestions on drying conditions from Mr. Carl Stark of J. P. Stevens Company, the following procedures were used in the plant production of the nonwoven fabrics.

a. Experimental Nonwoven Fabric 10-30-62R

This nonwoven fabric was made from 2.8-denier, 2.0-inch, Narcon No. 2, bright fibers. The weight of the unbonded web was 2.1 oz/yd^2.

The web was impregnated with a bath containing a 1:1 solids ratio of Rhoplex HA-12 and Rhoplex HA-8 and 0.5% Catalyst A, on the weight of the bath, to apply 1.4 oz/yd^2 of solids. This gave a bonded nonwoven fabric containing 60% fibers and 40% binder. The impregnated nonwoven fabric was dried for 3 minutes at 95°C, 3 minutes at 135°C, and 6 minutes at 150°C.

The bonded material was treated with a bath containing a mixture of Apex Flameproof 290B and FC-208 to apply 25% Apex Flameproof 290B solids and 3% FC-208 solids. The overpadded material was cured for 5 minutes at 150°C. The weight of the finished nonwoven fabric was expected to be 4.5 oz/yd^2, but it was 5.3 oz/yd^2, probably because of shrinkage.

One hundred yards of the rayon nonwoven fabric was prepared by J. P. Stevens Company by this procedure. Ninety-five yards of the finished nonwoven fabric was sent to the U. S. Army Natick Laboratories for evaluation and 5 yards was retained for our evaluation.

b. Experimental Nonwoven Fabric 10-30-62N

This nonwoven fabric was made from 2.3-denier, 2.0-inch nylon, semi-dull, Type 420 fibers. The weight of the unbonded web was 2.1 oz/yd^2.

The web was impregnated with a bath containing a 100:35 solids ratio of Geon 351 to Santicizer 141 (plasticizer) to apply 1.4 oz/yd^2 of solids. (The Santicizer 141 was added to the Geon 351 as a water emulsion containing 65% Santicizer 141.) This produced a bonded nonwoven fabric containing 60% fibers and 40% binder. The impregnated nonwoven fabric was dried for 3 minutes at 95°C, 3 minutes at 135°C, and 6 minutes at 150°C

The bonded material was then treated with a bath containing a mixture of Apex Flameproof 290B and FC-208 to apply 25% Apex Flamproof 290B solids and 3% FC-208 solids. The overpadded fabric was cured for 6 minutes at 150°C. The weight of the finished fabric was expected to be 4.5 oz/yd^2, but was 6.0 oz/yd^2, probably because of shrinkage.

One hundred yards of the nylon nonwoven fabric was prepared. Ninety-five yards of the finished nonwoven fabric was sent to the U. S. Army Natick Laboratories for in-house study and 5 yards was retained for our evaluation.

Mr. Carl Stark of J. P. Stevens Company reported that the webs of both the rayon and the nylon fibers had a high degree of loft and that the processing of the webs was complicated by electrostatic charges built up on the webs during laydown. These factors resulted in some non-uniformity; i.e., thick and thin spots. Also, the shrinkage of the fabric caused breaks. This was apparently a result of the low stretch of the high-tenacity nylon used in the fabric.

2. Properties

a. Physical properties

Table I-78 contains data on the physical properties of Experimental Nonwoven Fabric 10-30-62N and Experimental Nonwoven Fabric 10-30-62R. The properties of Experimental Paper 6-21-62R, which is the most promising paper material for the overgarment that we have found to date, are also given in the table, for comparison. Experimental Paper 6-21-62R is a 50:50 nylon-wood pulp paper reinforced with nylon scrim, treated with Rhoplex HA-12 for abrasion resistance, dyed OD, and treated with FC-208 to give resistance to liquid CW agents. A complete description of this paper is given in Section III-G.

Experimental Nonwoven Fabrics 10-30-62R and 10-30-62N were about equal in breaking strength, elongation at break, and air permeability, but Experimental Nonwoven Fabric 10-30-62N had higher tearing strength, abrasion resistance, and bursting strength. Experimental Nonwoven Fabric 10-30-62N weighed 6.1 oz/yd^2 compared to 5.4 oz/yd^2 for Experimental Nonwoven Fabric

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Table I-78. Physical Properties of Nonwoven Fabrics Made by J. P. Stevens Company

Material	Weight, oz/yd^2		Breaking strength, lb/in.		Elongation at break, %		Elmendorf tear, g		Abrasion resistance, cycles to rupture	Air permeability, ft^3/min/ft^2, 0.5 in. water	Bursting strength, psi	Stiffness, mg	
			Machine	Cross	Machine	Cross	Machine	Cross				Machine	Cross
Nonwoven Fabric 10-30-62 R	5.4	dry	21	18	25	24	1197	1356	847	222	79	142	115
		wet	12	10	25	27			879				
Nonwoven Fabric 10-30-62 N	6.1	dry	20	18	18	27	>3200	>3200	938	293	>120	>355	>355
		wet	13	18	30	44			765				
Experimental Paper 6-21-62 R	3.9	dry	31	18	20	26	1190	1190	356	16	87	113	119
		wet	25	14	23	26			207				

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10-30-62R, and this difference in weight may account for the superior properties. Experimental Nonwoven Fabric 10-30-62N was very stiff, and the surface was oily, probably due to migration of the plasticizer (Santicizer 141) to the surface. In comparison to Experimental Paper 6-21-62R, the nonwoven fabrics had lower breaking strengths in the machine direction, about the same elongations at break, and higher tearing strengths, resistances to abrasion, air permeabilities, and bursting strengths. The nonwoven fabrics were stiffer and heavier than the paper; thus, except for stiffness and weight, the physical properties of the nonwoven fabrics were generally better than those of Experimental Paper 6-21-62R.

b. Flame resistance

Experimental Nonwoven Fabric 10-30-62N had a char length of 5.4 inches as determined by the vertical flame test (ASTM Method D 625-55T). Three specimens of Nonwoven Fabric 10-30-62R burned to the end, but did not flame; however, when three additional specimens were evaluated, they had an average char length of 5.9 inches indicating that the flameproof agent was not evenly applied to this material. Apparently, either of these fabrics can be made to have acceptable flame resistance.

c. CW resistance

Table I-79 shows the resistances to liquid VX, HD, and GB agents of Experimental Nonwoven Fabrics 10-30-62N and 10-30-62R.

Experimental Nonwoven Fabric 10-30-62R was resistant to liquid VX and GB agents by the standard drop and expulsion test. One specimen of the fabric was penetrated by liquid HD in the expulsion test, but this specimen was taken from a thin portion of the material and is not considered to be representative of the fabric.

Experimental Nonwoven Fabric 10-30-62N was resistant to liquid GB agent by the standard drop and expulsion tests. Four of twelve drops of liquid VX agent penetrated the nylon fabric in the standard drop test, but there were no penetrations of the fabric by liquid VX agent in the expulsion test. There was no penetration of the fabric by liquid HD agent in the standard drop test, but 2 out of 8 specimens were penetrated in the expulsion test. The penetration of Experimental Nonwoven Fabric 10-30-62N by liquid CW agents was probably due to the non-uniformity of fabric thickness. The migration of the plasticizer used in the binder to the fabric surface probably affected the CW resistance of the fabric.

Table I-79. Resistance to Liquid CW Agents of Experimental Nonwoven Fabrics[a]

Fabric	VX			HD			GB		
	Drop test		Expulsion test	Drop test		Expulsion test	Drop test		Expulsion test
	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated
Experimental Nonwoven 10-30-62 N	2/2	4/12	0/8	0/2	0/12	2/8	0/2	0/12	0/8
Experimental Nonwoven 10-30-62 R	0/2	0/12	0/8	0/2	0/12	1/8	0/2	0/12	0/8

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[a] Specimens or drops penetrated/specimens or drops used; 7 to 8 mg drops.

IV. OVERGARMENT DESIGN STUDIES

The specifications for the design of an expendable overgarment required that it should:

fit over the clothing and equipment (except weapon) of a combat soldier and afford complete protection against liquid CW agents for a minimum of 6 hours,

be compatible with the soldier's clothing and equipment, including the gas mask,

have closures that would prevent entry of CW agents,

not reduce the efficiency of the soldier,

be easily donned and simple in design,

be required in a minimum number of sizes,

be capable of being carried in the soldier's load-carrying equipment or pocket,

be as tight fitting as possible in order to reduce the silhouette of the soldier and the tendency for the garment to be snagged,

lend itself to low-cost mass-production techniques.

Work on the design of the overgarment was begun at Southern Research Institute and then continued by International Latex Corporation, Dover, Delaware, under a subcontract D-7933. One- and two-piece overgarment designs, sleeve modifications, methods of forming seams, different types of closures and fabrication of protective gloves and boots were studied. Designs by International Latex Corporation were approved by the Project Officer, and garments were fabricated from two experimental papers and delivered to U. S. Army Natick Laboratories for field evaluation.

A. Two-piece Protective Overgarment Design Studies at Southern Research Institute

The basic design of the Chemical Warfare Protective Garment described by Purchase Descriptions IP/DES S-29-0 and IP/DES S-27-0 was first examined for suitability for the expendable overgarment. This garment consisted of pajama-type trousers with draw strings at the waist and ankles and a long coat with a Pullman closure and tails. The tails of the coat wrapped around the thighs and were tied with draw strings. The basic design of this garment is shown in Figures I-2, I-3, and I-4.

An overgarment of this design was made from Kaycel 100 with sewed seams to determine what modifications might be necessary in making the garment from paper. A paper overgarment with glued seams and incorporating several modifications was then fabricated from Kaycel 100 for further study. The final modified designs for the coat and pants are shown in Figures I-5 and I-6, respectively. The modifications in the basic design were: (1) glued seams were used to eliminate stitching, and the back seam in the coat was eliminated; (2) the buttons of the Pullman closure were replaced by Velcro tape and an aluminum zipper; (3) the waist drawstring of the coat was moved outside for use as a belt, and belt holders were sealed to the waist of the garment; (4) the waist drawstring in the pants was replaced with elastic; (5) the drawstring eyelets in the bottoms of the pants legs were eliminated by leaving the drawstring tunnels open on both ends; and (6) the apex of the V in the tail of the coat was reinforced.

The modifications made in the garment are discussed below:

Seams: All seams of the basic design were sewn, flat-felled seams. Stitching of the seams of the paper garment was very difficult; the paper stretched during sewing and tended to tear away from the stitches. Because of the difficulty in obtaining good seams by sewing, the modified garment was made with glued seams. Splic-It, which was found previously to make seams stronger than the paper, was used as the adhesive. Another reason for the use of glued seams was go make them more impervious to liquid CW agents. Also, it was felt that stichless seams would allow the garment to be fabrica by automated production facilities.

The seam in the back of the coat was eliminated to decrease the nu of seams susceptible to CW penetration and to decrease the number of fabricating operations.

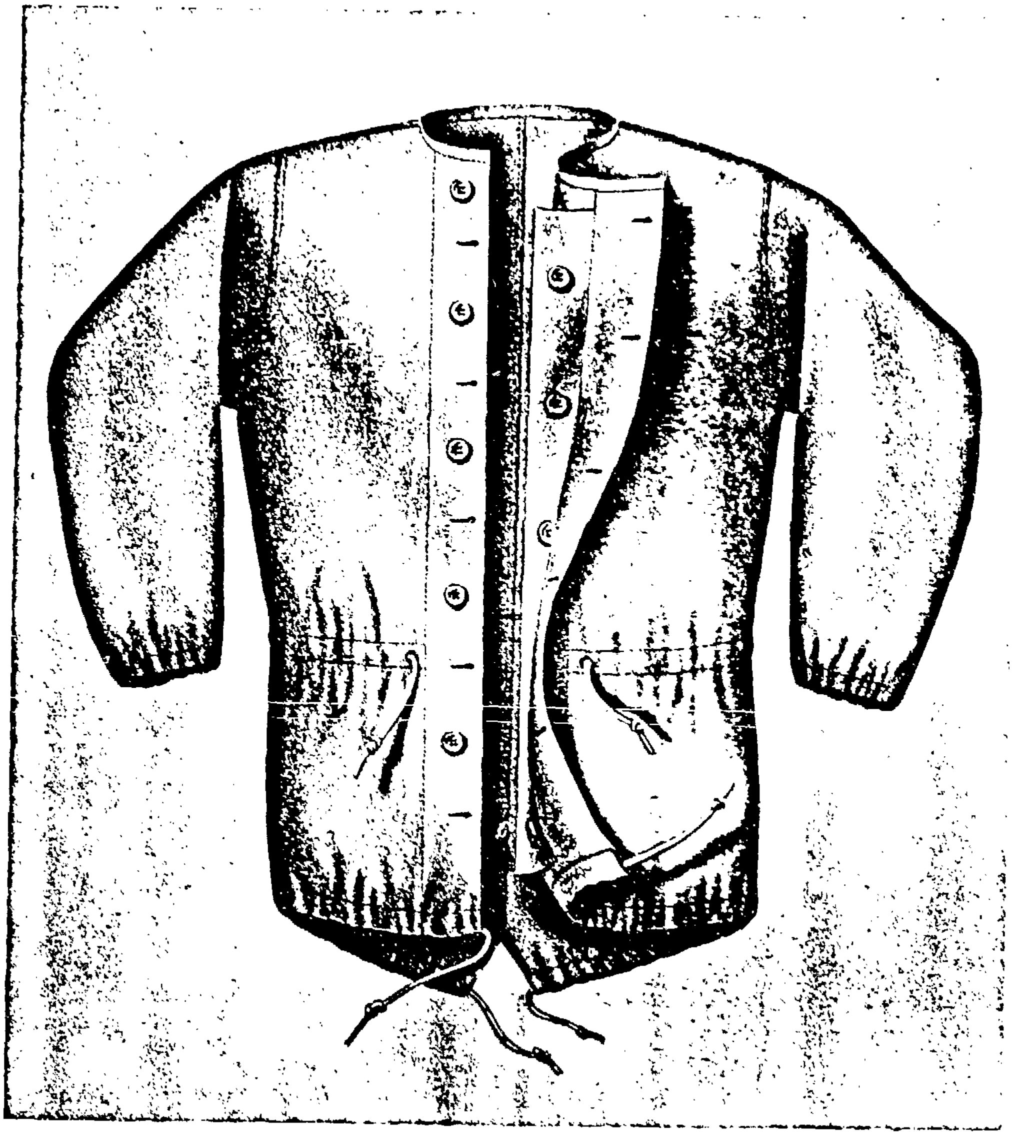

Figure I-2. Basic Design of Two-Piece Protective Overgarment—Front of Coat

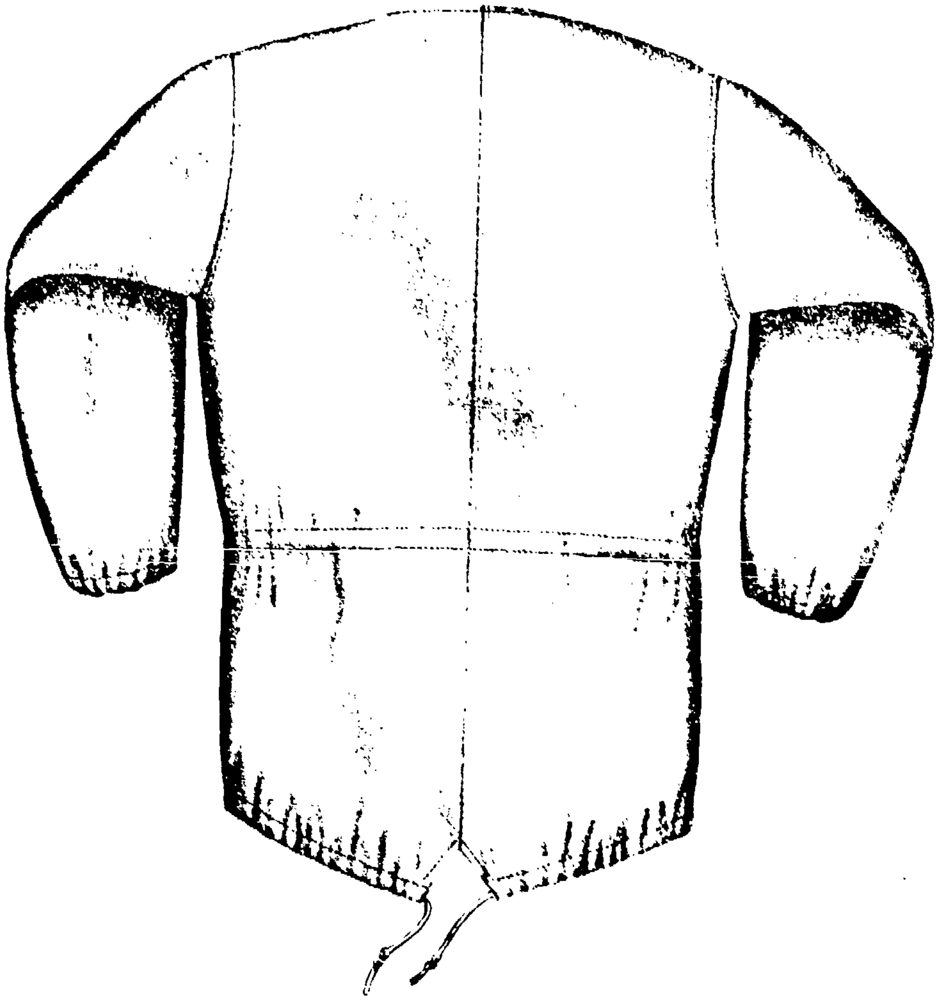

Figure I-3. Basic Design of Two-Piece Protective Overgarment—Back of Coat

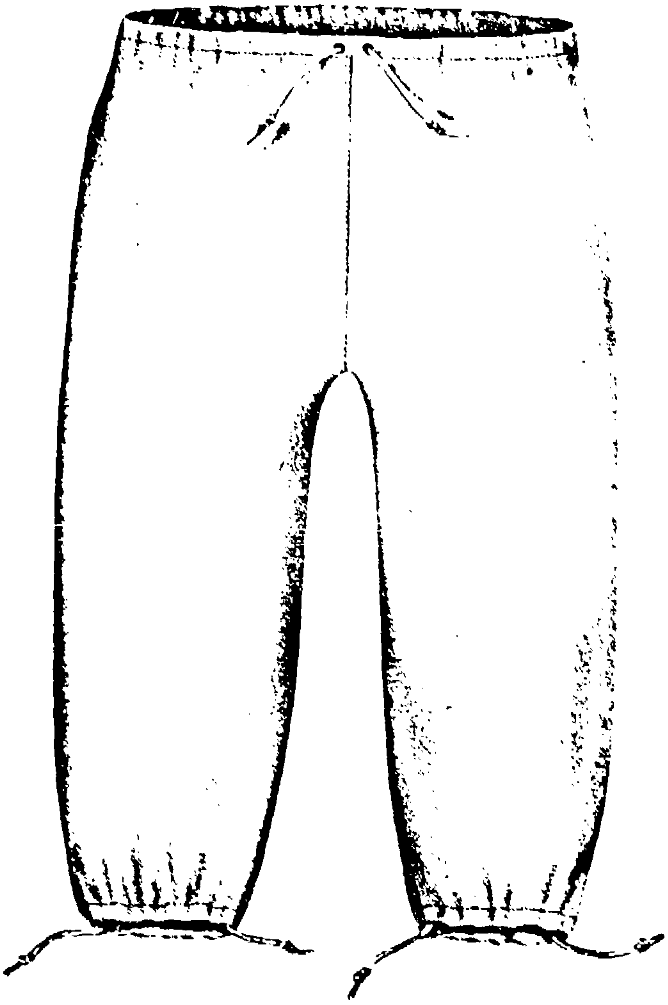

Figure I-4. Basic Design of Two-Piece Protective Overgarment — Pants

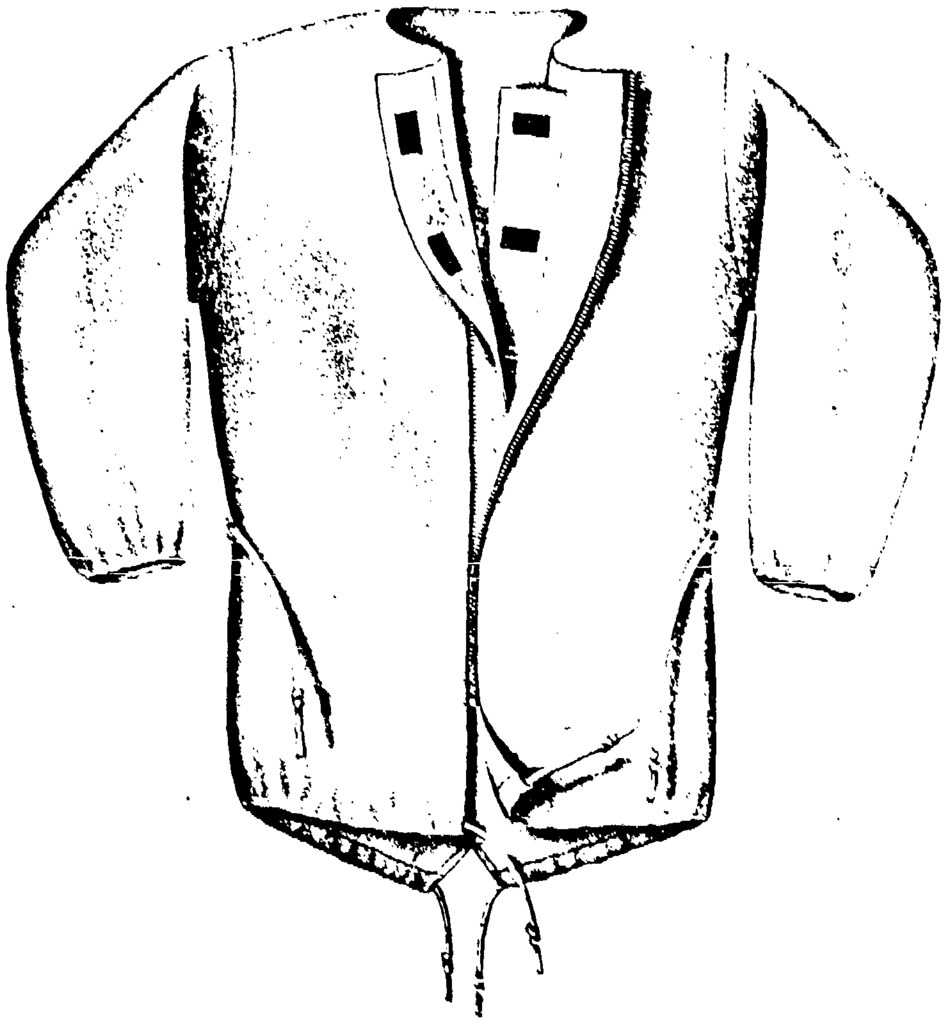

Figure I-5. Modified Design of Two-Piece Protective Overgarment—Coat

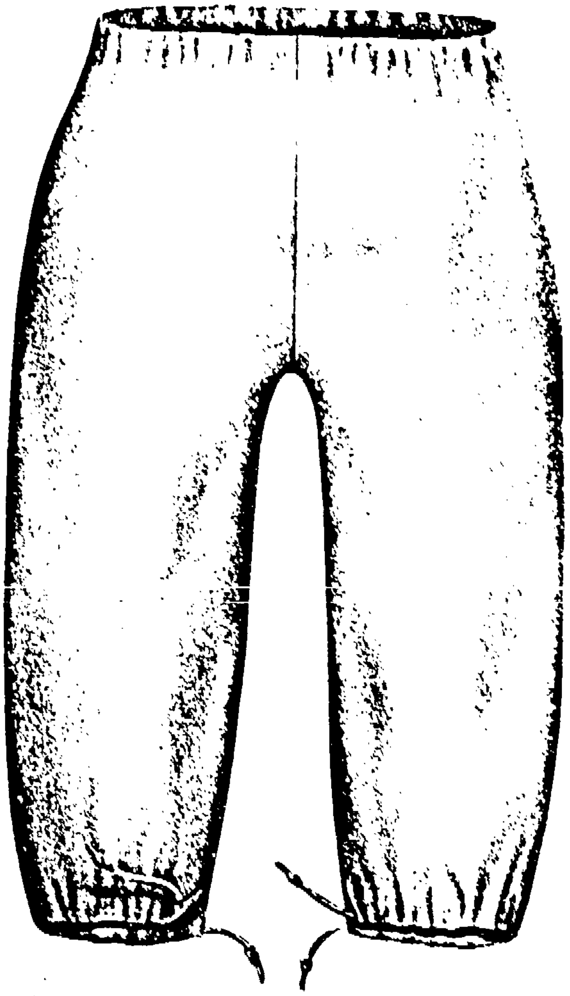

Figure I-6. Modified Design of Two-Piece Protective Overgarment—Pants

Pullman closure: No attempt was made to change the general design of the Pullman closure, which is shown in Figure I-2, since this type of closure is known to provide adequate protection against liquid CW agents. However, in the modified design, an aluminum zipper was used on the outer flap of the Pullman closure and 1 x 1-inch sections of Velcro tape were used in the flap of the closure in place of buttons. Both the zipper and the Velcro tape were sealed to the paper with Splic-It. The zipper and Velcro tape eliminated the several major objections to the use of buttons, which were: closures could not be made rapidly with them, garments with buttons would be difficult to make with automated equipment, buttons could be easily snagged and torn from the garment, and button holes would have to be reinforced.

Other types of fasteners were also tried:

Standard metal grippers were put on cotton twill tape, and the tape was glued to the paper coat with Splic-It. It was impossible to fasten the Pullman closure rapidly with the grippers and the grippers were heavy, weighing about 1.7 g each.

Strips of Velcro tape 1-inch wide were sealed with Splic-It to the outer flaps of the Pullman closure. The tape, which ran the length of the closure, formed a tight continuous seal, but it was difficult to align the two strips of tape and this was necessary to obtain tight closure.

A lightweight zipper made of monofilament-nylon (Talon Zephyr) could be closed rapidly and did not snag the paper when zipped. This type of zipper appeared to be well suited for our needs, but the zipper was not manufactured in the length or the separating type that was needed for the coat.

Drawstrings: In the basic design, drawstrings were used at the waist and tails of the coat (see Figure I-2) and at the wrist and ankles of the pants (see Figure I-3). The drawstrings were in tunnels and metal eyelets were used as outlets for all the tunnels, except those at the tails of the coat which were open at the ends.

The metal eyelets in the first garment made for this study pulled out of the paper when the drawstring was drawn and tied, so attempts were made to increase the strength of the paper at the points where metal eyelet were used in the overgarment. Rhoplex B-15, an acrylic binder, was pai on these areas before and after inserting eyelets, but this was not effectiv Reinforcing the paper with masking tape was not beneficial nor was gluing thicknesses of the Kaycel to the garment at the points where the eyelets we inserted.

To eliminate the problem with the metal eyelets, the waist drawstring of the coat was moved to the outside of the coat for use as a belt. Belt loops made from paper were sealed to the waist of the coat. The drawstring in the waist of the pants was replaced with elastic, and the drawstring eyelets at the bottoms of the pants legs were eliminated by leaving the tunnels open at both ends.

<u>Coat sleeves</u>: Set-in type sleeves were used in the basic design, and there were darts at the elbow of each sleeve. The wrists of the sleeve contained elastic.

One modified coat was made with Raglan sleeves (see Figure I-7) instead of the set-in sleeves. This type of sleeve was investigated because it had no seam at the shoulder, where the garment would be frequently subjected to high stresses. However, it was found that the Raglan sleeve removed fullness from the shoulder of the coat, restricting arm movement and, consequently, this sleeve did not appear desirable.

The results of field studies by U. S. Army Natick Laboratories of paper garments with sewn set-in sleeves showed that the paper at the seam was frequently pulled loose from the stitching. Since the glued seams had strengths greater than that of the paper, no problem was anticipated with set-in sleeves in the modified design.

The modified two-piece overgarment met most of the general desi characteristics for the protective overgarment, but it could not be donned rapidly, and it was felt that automated fabrication of the garment would be difficult.

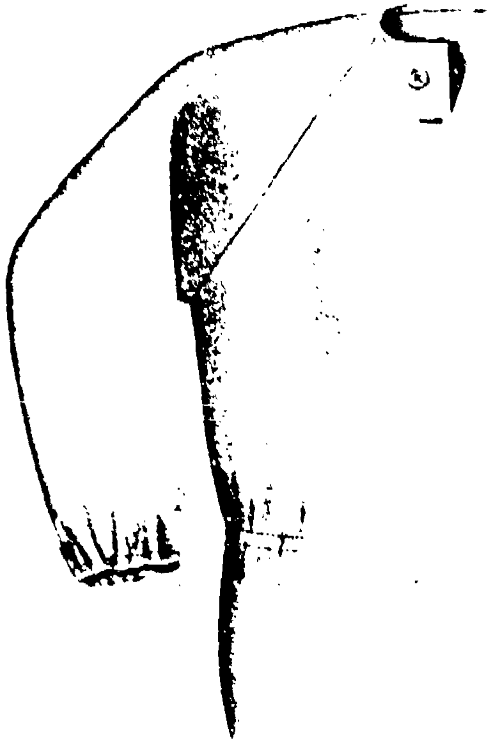

Figure I-7. Raglan Sleeve

B. One-Piece Protective Overgarment Design Studies at Southern Research Institute

A one-piece overgarment appeared to offer better possibilities for quick donning and automated fabrication than a two-piece overgarment. Also, a one-piece overgarment was expected to require less material, thus reducing the cost and weight of the garment.

The one-piece overgarment shown in Figure I-8 was made from Kaycel 100 with glued seams. It had a Pullman closure on the inside of the trouser legs that was similar to the Pullman closure used in the coat of the modified two-piece overgarment. Pieces of heat-sealable paper tape containing lightweight grippers were bonded to the sleeves at the wrists. This tape could be drawn tightly around the wrist and snapped to make a tight closure, but the tape broke easily and was not recommended for use in the overgarment. The ankle closures were made with pressure-sensitive polyethylene tape. The tape had a protective paper covering which was only removed for a 2-inch length, and this portion of the tape was sealed to the garment. The remainder of the protective covering was to be removed from the tape after the garment was donned and sealed around the leg.

A combat-loaded soldier would have difficulty in donning the garment as he would have to pull it over his head and load-carrying equipment. It would also be extremely difficult for him to make the closure located on the inner sides of the pants legs. The grippers used at the wrists were not satisfactory, but they could be replaced with pressure-sensitive tape. Pressure-sensitive tape at the wrists and the ankles of the protectiver overgarment was preferred over grippers, elastic, or drawstrings. Strong, tight closures could be made rapidly with tape, and the tape was easily applied to the garment.

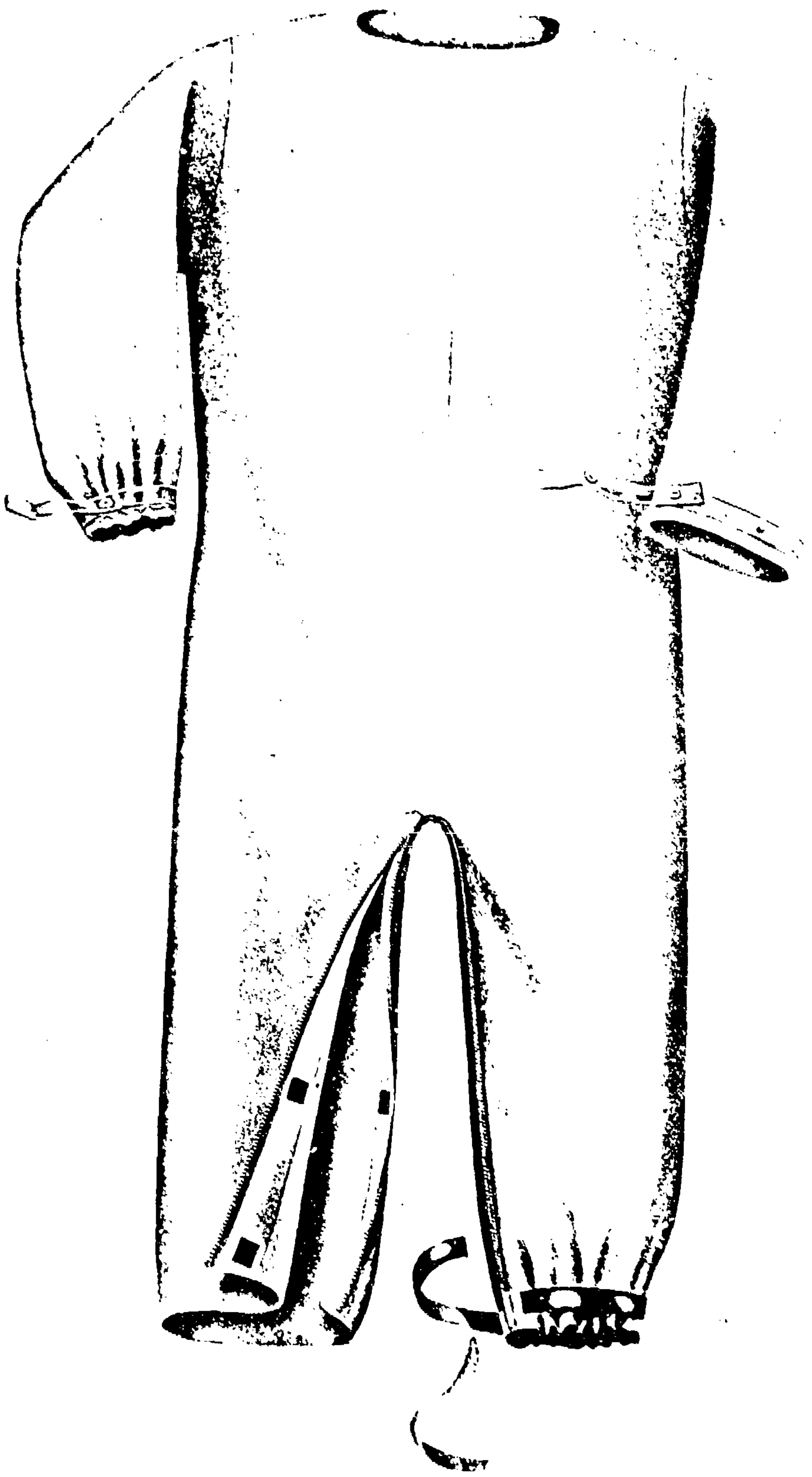

Figure I-8. Design of One-Piece Protective Overgarment

[redacted]

Another one-piece overgarment was made as shown in Figures I-9 through I-12. This garment was essentially a long coat with a tail that was actually the front of the garment. The garment was made from Kaycel 100 with seams glued with Splic-It. The garment had two Pullman closures at the front. The design of the Pullman closures, which can best be seen in Figure I-12, was the same as that used in the overgarment previously developed. The inner flaps of the Pullman closures were held together with 1 x 1 inch sections of Velcro tape, and the outer flaps were joined with aluminum zippers. The inner flaps of the closures were on the tail portion of the garment. Both the zipper and the Velcro tape were sealed to the paper with Splic-It. The sleeves were the set-in type and the wrists and ankles contained elastic.

This garment was put on like a coat (Figure I-10) and the tail was brought between the legs and fastened at the front with Velcro tape as shown in Figure I-11. The closures were then made with the zippers to form the front center and legs of the garment as shown in Figures I-12 and I-9.

The chief advantage of this overgarment was that it could be easily and quickly donned. There was nothing for the soldier to put over his head or for him to step into. There were only two closures to be made. The chief disadvantage of the overgarment was the complicated design. Attempts were made to replace the set-in sleeve of the overgarment with a modified sleeve and these are discussed in the following section. Lightweight adjustable straps were investigated as replacements for the elastic in the wrists and ankles and reversal of the zippers was planned so they could be started at the top while a man was standing.

Studies were initiated on a one-piece overgarment that was similar to a pair of men's coveralls, except that it had bell-bottom legs to facilitate donning; but the studies were terminated at an early stage of the work because similar work was started by International Latex Corporation.

[redacted]

Figure I-9. One-Piece Protective Overgarment

Figure I-10. First Step in Donning Protective Overgarment

Figure I-11. Second Step in Donning Protective Overgarment

Figure I-12. Third Step in Donning Protective Overgarment

C. Sleeve Studies

Attempts were made to improve the sleeve design of the overgarment. A set-in sleeve gave the wearer complete arm mobility, but the sleeve would be difficult to insert by semi-automated production techniques. The Raglan sleeve was simpler in design than the set-in sleeve, but it was difficult to make it wrinkle-free with paper materials.

One type of sleeve studied was an integral part of the garment. Half of the sleeve was part of the front portion of the garment, the other half was part of the back portion of the garment. This sleeve was formed when the back and front portions of the garment were joined with a seam from neck to wrist and from wrist to waist. The sleeve had a bat-wing appearance when extended horizontally.

Efforts were made to eliminate the excess fabric in the armpit by stitching a V in the armpit area and then clipping up the center of the V, but this only partially eliminated bunching of the fabric under the arm. One bat-wing type sleeve was made with a gusset in the armpit. The gusset eliminated some of the excess fabric under the arm, but it complicated the design. Neither of the sleeves studied was believed suitable for use in the overgarment.

A partial Raglan sleeve was made that was the Raglan type in the back and the set-in type in the front. This sleeve eliminated the fullness of the Raglan sleeve under the arm, and allowed more freedom of motion than the Raglan sleeve. The front portion of this sleeve was much easier to insert than a full set-in sleeve. The disadvantage of the partial Raglan sleeve was that it required more cut-out time and excessive seaming.

No further work was done on sleeve design because of the start of design by International Latex Corporation.

D. Seam Studies

Sewn seams of overgarments made from some papers do not withstand simulated combat service, as shown by field evaluations made by the U. S. Army Natick Laboratories. Therefore, studies were undertaken to determine if glued seams or ultrasonic-bonded seams could be used.

1. Glued seams

Seventeen adhesives, which are described in Table I-80, were evaluated for making the seams for the overgarment. An area 1-inch wide along the edge of one sheet of reinforced nylon-wood pulp paper was coated with the adhesive. The edge of another sheet of like paper, which was not coated, was placed over the adhesive-treated area of the first paper to make a 1-inch overlap seam. All of the 1-inch overlap seams, except those prepared with Vultex 1-S-1009 and PR-153 which were ineffective, had separation strengths greater than the strength of the paper.

One-inch flat open seams were prepared with some of the adhesive The flat open seams were prepared as follows: 1-inch strips along the edge of two sheets of the paper were coated with the adhesive, and the adhesive-coated area of one sheet of the paper was pressed on the adhesive-coated area of the second sheet of paper. The values for the peel strengths of thei seams are given in Table I-80. EC-1729, N-159, Bostick 4034, and Herculite CVV produced seams with high peel strength. Herculite CVV, however, was found to have too short a tack time for use in garment fabrication.

Overlap seams made with EC-1729, Bostick 4034, and N-159 were evaluated for resistance to liquid HD, GB, and VX agents by the standard drop and expulsion tests. As shown in Table I-81, there was no significant penetration of the seams by any of the agents.

As a result of the good CW resistance and strength of seams made with EC-1729, Bostik 4034, and N-159 these adhesives were considered satisfactory for making the seams of the protective overgarment.

[illegible]

Adhesive	Producer	Type	Solids content, % by weight	Peel strength,[a] lb/in.	Comments
Polyester 46971[b]	E.I. du Pont de Nemours & Co.	polyester in 1,1,2-trichloroethane	15	4.3	odorless, melting range 78-100°C
EC-1729	Minnesota Mining & Mfg. Co.	synthetic rubber based	-	7.4	
EC-784[b]	Minnesota Mining & Mfg. Co.	oil-soluble elastomer in water	60	4.4	reactivator:petroleum naphtha
SWB-952[b] (A&B)	Interchemical Corp., Angiers Adhesives Dept.	neoprene in solvent[c]	24	2.5	
EZ-1904[b]	Permacel Adhesives	vinyl chloride in solvent	38	4.5	reactivator: methyl-ethyl-ketone
Bostik 4034[b]	B&B Chemical Co.	synthetic rubber resin in solvent	35	5.7	reactivator: Bostik 317 cr acetone
CV-794[b]	Borden Chemical Co.	vinyl emulsion type	49	1.9	thinner: water
CVV[b,d]	Herculite Protective Fabrics		-	6.0	reactivator: methyl-ethyl-ketone
N-159[b]	Union Bay-State Chemical Co.	neoprene in solvent	23	6.3	flash point -7 to 4°C, reactivator: toluene
Rubba X-210-B[b]	Adhesive Products Corp. (Rubba Adhesives)	latex in water	60	5.1	reactivator: toluene
Formica contact cement	American Cyanamid Co.	solvent based	27		thinner: 2-butanone
Splic-It	Borden Chemical Co.	latex in water	93		thinner: water
Vultex 1-S-1052	General Latex & Chemical Co.	latex in water	64		
Vultex 1-S-1009	General Latex & Chemical Co.	latex in water	57		thinner: water
ARCCO S-377	Borden Chemical Co.	vinylchloride acetate copolymer	-		paste
U.S. Royal Industrial Adhesive M 6256	U. S. Rubber Co.	thermoplastic resin	90		
PR-153	Borden Chemical Co.	resinous glue	100		soluble in water plus ethanol

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[a] Experimental Paper 2-2-62 (50:50 nylon-wood pulp paper containing Rhoplex B-15) was used for these studies.

[b] Supplied by International Latex Corporation; all other adhesives obtained from producer.

[c] Unspecified solvent indicates one or more solvents other than water are utilized.

[d] Herculite CVV was recently developed and no specifications sheet has been tabulated.

[redacted]

Table I-81. CW Resistance of Seams

	HD			GB			VX		
	Drop test[a]		Expulsion test[b]	Drop test[a]		Expulsion test[b]	Drop test[a]		Expulsion test[b]
Adhesive or method	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated	Specimens penetrated	Drops penetrated	Specimens penetrated
EC-1729	1	(3)[c]	0	0	0	0	0	0	0
Bostik 4034	1	(1)[c]	0	0	0	0	0	0	0
N-159	0	(1)[c]	0	0	0	0	0	0	0
Ultrasonic seams	1	6	-	1	6	-	1	6	-

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[a] Duration of drop test was 6 hours; 1 specimen was tested with 6 drops per specimen, 7 to 8 mg drops.

[b] Duration of expulsion test was 1 minute; 3 specimens were tested with 1 drop per specimen, 7 to 8 mg drops.

[c] Pin-point penetrations.

[redacted]

2. Scaled seams

Overlap seams were made on a nylon-wood pulp paper containing Rhoplex B-15 and FC-208 (Esperimental Paper 2-2-62) by means of an ultrasonic sealer. The resistances of the seams to liquid HD, GB, and VX agents were determined by the standard drop and expulsion tests. The data given in Table I-81 show that the ultrasonic seams were penetrated by all of the agents and therefore were not considered satisfactory for use in the overgarment.

E. Plastics for Boots and Gloves

Plastic films were evaluated for use in protective gloves and boot coverings because of their cheapness, good abrasion resistance, and heat sealability.

Table I-82 gives data on the CW resistance of plastics that were considered to be the most resistant to HD, L, GA, GB, and VX agents, as determined from the literature. Comments on the breaking and tearing strengths of each type of plastic are given in the table. It was concluded that the polyamides, polyethylene, and Mylar were the best plastics for use in making gloves and boot coverings since they had good CW resistance and might be heat sealable to the overgarment.

A pair of polyethylene boots supplied by the United States Army Natick Laboratories was evaluated for resistance to liquid HD, GA, and VX agents. Specimens cut from the sole and from the top of the boots (to include a seam) were not penetrated by any of the agents in the standard drop test, but there were slight indications of swelling by VX and HD agents.

Samples of Mylar, polyethylene film, nylon film, and the polyethylene boots were heat sealed to a piece of 50:50 nylon-wood pulp paper reinforced with 100 denier nylon scrim and containing 25% Rhoplex B-15 solids. A Vertrcd Thermal-Impulse-Sealer was used to make the seals. Data on the optimum setting required to make a good seal and on the peel strengths of the best obtainable seals are given in Table I-83.

[redacted]

[redacted]

Table 1-82. CW Resistance and General Properties of Plastic Films[a]

	CW Resistance						
	HD	L	GA	GB	VX	Properties	Comments
Polytetrafluoroethylene	1	-	1	1	1	low tearing strength low tensile strength	expensive; no known adhesive for bonding; non-heat sealable
Polytrifluoroethylene (2 mil)	1	-	1	1	1	low tearing strength fair tensile strength	expensive; no known adhesive for bonding; poor dimensional stability
Poly(ethylene terephthalate) (2 mil)	1	1	1	1	1	very low tearing strength good tensile strength	poor heat sealability
Polyamides						good tensile strength good tearing strength	economical
Type 8	2	-	1	1	1		
Type 610	-	-	-	good	good		
Type 66	-	-	-	good	good		
Type 6	-	-	-	good	good		
Polyethylene						low tensile strength low tearing strength	economical, good heat sealability
Low density	-	-	-	good	fair		
High density	-	-	-	good	good		
Polyvinylidene chloride (4 mil)	3	3	2	2	-	good tensile strength poor tearing strength	poor heat sealability

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[a] Data for CW resistance of polyethylene and polyamides except type 8 were taken from C. E. Collins, "Plastics Data Book," U. S. Army Chemical Warfare Laboratories, Army Chemical Center, Maryland, pp. 33-41 (1959).

Data for CW resistance of all other plastics were taken from Engineering Proposal for Protective Overgarment, International Latex Corporation, Industrial Products Division, Research and Development Department, Dover, Delaware, May 11, 1961.

Test conditions: Liquid agent in a closed cup placed on outer surface and time measured to penetration of about 1 mg/sq cm of agent. *HD* test run at 35°C—others at room temperature.

Penetration time ratings

1 - greater than 1 day.
2 - greater than 5 hours and less than 1 day.
3 - greater than 1.5 hour and less than 5 hours.

[redacted]

[redacted]

Table I-83. Optimum Heat Setting Conditions for Sealing Plastic Films to 50:50 Nylon-Paper and Peel Strength of Optimum Seal

Plastic	Manufacturer	Thickness, mils	Seal strength at setting									Seal strength, lb/in.
			2	3	4	5	6	7	8	9	10	
Polyethylene (high density)	Visking Company	5				poor	poor		fair	fair	fair	
Polyethylene (high density)	Visking Company	10	none			none			none		none	
Polyethylene	Du Pont Company	3				none					none	
Polyethylene boots	b	8.4							poor		good	5.1[a]
Nylon	Polymer Corp. of Pennsylvania	3							fair		good	4.7[a]
Nylon	Polymer Corp. of Pennsylvania	5	none			none			poor		poor	
Mylar	Du Pont Company	1	poor		fair	good		good	burns			
Mylar	Du Pont Company	5							fair		good	5.1[a]

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[a] Sealed at setting of 10.

b Boots obtained from United States Army Natick Laboratories and given to them by Naval Radiological Defense Laboratory.

[redacted]

[redacted]

The 3-mil nylon, the 5-mil Mylar, and the 8.4-mil polyethylene from the boot all gave peel strengths of approximately 5 lb/in. width when sealed to the nylon-wood pulp paper. On the basis of breaking and tearing strengths, heat sealability, and resistance to CW agents, it was concluded that nylon would be the best plastic for use in gloves and boot coverings. Polyethylene would not have as good physical properties as nylon, but would have the advantage of lower cost. These studies were continued by U. S. Army Natick Laboratories.

F. Design Studies by International Latex Corporation

International Latex Corporation of Dover, Delaware, was given a subcontract (D-7933) to develop four designs for a protective overgarment, including gloves and boots. The designs were needed for fabrication of overgarments to be field evaluated by the U. S. Army Natick Laboratories.

Designs incorporating all of the best features of various modifications were established for one-piece, pajama-type and two-piece, coverall type overgarments and for boots and gloves to be worn with the overgarments. Overgarments were fabricated, according to the approved designs, from two experimental nylon scrim-reinforced nylon-wood pulp papers, 6-21-62GCD and 6-21-62R. Gloves and boots were made from polyethylene and from poly(vinyl chloride). The overgarments, gloves, and boots itemized from Table I-84 were delivered to the U. S. Army Natick Laboratories for field evaluation.

The seams in the overgarments were sewn and then painted with an adhesive. These seams had satisfactory CW resistance as determined by the Chemical Corps. The modified Pullman closure used in the one-piece overgarment was also satisfactory for CW resistance.

Field studies of the overgarments indicated that the one-piece design was more desirable.

The design work done by International Latex Corporation is described in their progress reports dated June 12, July 12, September 24, September 25, and October 12, 1962, and in their final report dated December 12, 1962. Copies of these reports were sent to the Project Officer at U. S. Army Natick Laboratories.

[redacted]

[redacted]

Table I-84. Protective Overgarments Fabricated by International Latex Corporation

Design	Number of pieces	Description Gloves	 Boots	 Paper	Items fabricated
ILC	1	separate	attached	6-21-62 GCD[a]	11
ILC	1	separate	separate	6-21-62 GCD	11
ILC	1	separate	separate	6-21-62 R[b]	20
ILC	2	separate	attached	6-21-62 GCD	11
ILC	2	separate	separate	6-21-62 GCD	11
USANL[c]	2	separate	attached	6-21-62 GCD	11
USANL[c]	2	separate	separate	6-21-62 GCD	11

[a] Scrim reinforced nylon-wood pulp paper containing 25% Geon 577 and 13% antimony trioxide on weight of untreated paper and 3% FC-208 solids on weight of Geon-antimony trioxide treated paper.

[b] Scrim reinforced nylon-wood pulp paper containing 25% Rhoplex HA-12 on weight of untreated paper and 2.5% FC-208 on weight of Rhoplex-treated paper.

[c] U. S. Army Natick Laboratories.

[redacted]

PART II. DEVELOPMENT OF MATERIALS FOR AN OVERGARMENT PROVIDING PROTECTION AGAINST LIQUID, VAPOR, AND AEROSOL

I. INTRODUCTION

Part I of this report describes the development of an overgarment intended to be serviceable and to provide protection against liquid CW agents for a minimum of six hours. Part II describes work aimed at the development of materials for an overgarment intended to be sufficiently durable for wear for three to twenty-one days and to provide protection against CW agents for a minimum of six hours during this period. Initially, it was required that the more durable overgarment protect against GB, VX, and HD in liquid, vapor, and aerosol forms. Later, the requirement for protection against aerosols was dropped; and, with this change, the direction of the experimental work also changed. Therefore, the development of materials for an overgarment protecting against liquids and vapors only is described separately in Part III.

Most of the work to be described in Part II was based on the concept of a three-layer garment. The outer layer was intended to provide resistance to penetration by liquid agents and most of the resistance to wear. The middle layer was intended to entrap aerosol droplets. The inner layer was intended to prevent the penetration of vapor by chemically converting agent vapor to a non-toxic form with a reactive impregnant. The three layers were to be fastened together by stitching or by adhesives. Some work was also done on one-layer and two-layer systems combining the protective functions of the three separate layers.

II. SUMMARY

Evaluation of several materials for the outer layer of a three-layer overgarment intended to provide protection against CW agents in liquid, aerosol, and vapor form, indicated that a 5.5-oz/yd^2 nylon-cotton oxford fabric proved best. This fabric, when treated with Quarpel, provided adequate resistance to penetration by liquid CW agents. Its physical properties indicated that it would be sufficiently durable for three day's wear.

For the middle layer, which would function primarily as an aerosol filter, a 1-oz/yd^2 paper made of Dacron and glass fibers was satisfactory. Liner E-18, a U. S. Army material composed of glass, viscose, and Vinyon fibers, was also satisfactory; but it had a greater weight, 3.7 oz/yd

For the vapor-absorbing inner layer, a 1.9-oz/yd^2 rayon (Narcon) nonwoven fabric treated with S-330 and Hycar 4501 appeared to be the most suitable. A treated 1.8-oz/yd^2 Fortisan fabric was also suitable, except for low air permeability, but this was partially compensated for by its high moisture-vapor permeability.

Of several combinations investigated as systems for a two-layer garment, a composite of the 5.5-oz/yd^2 oxford cloth and the treated Fortisa fabric offered the best protection. However, the air permeability of the composite was low.

A theoretical study of the effects of fiber diameter, mat thickness, and bulk density on aerosol filtration efficiency indicated that a single fabri layer, suitably treated, might be useful as a protective garment. To substantiate this hypothesis, it was determined by experiment that the aerosol retention of certain paper filters was not appreciably affected by increased binder content, and that air permeability was only slightly decreased.

III. EVALUATION OF MATERIALS FOR THREE-LAYER OVERGARMENTS

A. Outer Layer

Materials to be evaluated for the outer layer were chosen primarily on the basis of their probable wear-resistance, weight, and air permeability. These materials were treated with FC-208 or Quarpel to make them non-wettable by liquid agents. Both woven and nonwoven materials were included.

Nylon parachute fabric. Lightweight woven fabrics are generally not resistant to penetration by liquid agents, even when treated with FC-208, because of the open-weave construction. For example, five out of six drops of VX penetrated a 1.1-oz/yd^2 nylon parachute fabric containing 4% of FC-208 solids. To reduce the size of the open spaces, the nylon fabric was heated in a press at 230°C and 1500 psi with Teflon sheeting between the fabric and the press platens. This treatment reduced the air permeability from 88 ft^3/min/ft^2 to about 40 ft^3/min/ft^2. FC-208 was applied to some samples before hot-pressing and to others after hot-pressing. Although the hot-pressed fabric acquired increased resistance to penetration by liquid VX, it was still inadequate for protection.

Nylon oxford cloth. A nylon oxford cloth (3.0 oz/yd^2), padded with FC-208 to apply 4% solids and cured for 6 minutes at 150°C, was resistant to penetration by VX in the standard drop test, but not in the expulsion test. Hot pressing the treated fabric at 20,000 psi and at 150°C and 230°C did not improve its performance in the expulsion test.

Fortisan fabric. A 1.8-oz/yd^2 Fortisan fabric having a rip-stop weave was treated and hot-pressed in the same manner as the nylon fabrics but was not resistant to penetration by VX.

Nylon-cotton fabric. A 5.5-oz/yd^2 Quarpel-treated oxford fabric with cotton warp and nylon filling supplied by the U. S. Army Natick Laboratories was not penetrated by GB, VX, HD, or bis(2-ethylhexyl) hydrogen phosphite in the standard drop test, but it was penetrated by all three agents in the expulsion test.

Experimental paper 6-21-62R. This material, a nylon-reinforced 50:50 nylon-wood pulp paper impregnated with Rhoplex HA-12 and over-treated with FC-208, was not penetrated by any of the agents in either the drop test or the expulsion test.

Nonwoven rayon and nylon fabrics. The two fabrics made by the J. P. Stevens Company [10-30-62R (rayon), and 10-30-62N (nylon), Part I, Section III] were intended for use in an expendable garment, but were also considered for the outer layer of a durable garment. These materials had good resistance to penetration by GB, VX, and HD and also had good physical properties.

B. Middle Layer

The primary requirement for the middle layer of a three-layer garment was that it should be an efficient filter for liquid aerosol particles. This layer was to provide protection against aerosol particles averaging 2.5 microns in diameter for a minimum of 6 hours. The protection was required at a pressure differential of 0.1 in. of water. Secondary factors included weight, thickness, and air permeability. Strength was of minor importance. The experimental work included evaluation of nonwoven fabrics, battings (unbonded nonwoven webs), and papers for aerosol retention and certain other physical properties. Related work on aerosol filtration is described in Section IV in connection with studies on a one-layer system for protection against liquids, vapors, and aerosols.

Table II-1 gives the fiber compositions, weights, thicknesses, air permeabilities, and aerosol retentions of several materials. Some of the materials were so porous that two layers were used to determine the aerosol retention values. In such instances, two layers were also used in the determination of air permeabilities. Comments on those materials having more than 80% aerosol retention follow.

The glass-fiber paper, Type 1106-B, was eliminated from consideration because of its brittleness. The Type 5 paper and the handsheet made from Type 6 paper were retentive but were heavier than some of the other mixed-fiber materials made with glass fibers instead of asbestos.

Table II-1. Physical Properties of Materials Evaluated for Middle Layer

Type of material	Fiber composition	Weight, oz/yd²	Thickness, in.	Air permeability, ft³/min/ft², 0.5 in. water	Aerosol retention, %
Batt	50% nylon 50% Narcon	1.9	0.014	285[a]	7
Nonwoven	32% nylon[b] 32% Narcon	3.5	0.008	12	40
Batt	50% nylon 50% Narcon	2.4	0.020	235[a]	12
Nonwoven	32% nylon[b] 32% Narcon	3.8	0.008	12	40
Batt	100% Narcon	1.9	0.017	225[a]	13
Batt	100% viscose	3.0	0.032	370[a]	19
Batt	100% acetate	2.7	0.025	430[a]	2
Nonwoven, Pellon 970-W	unknown	2.2	0.013	175[a]	40
Nonwoven, Pellon 900-mat	unknown	1.5	0.010	210[a]	23
Paper, Type 1106-B	93% glass[c]	1.6	0.013	3	89
Paper, Type 5[d]	asbestos, hemp, viscose, cotton	4.0	0.023	30	91
Paper, made from Type 6[d]	asbestos, hemp, cotton, esparto	3.4	0.014	4	98
Batt	100% Dacron	2.5	0.018	370[a]	18
Liner E-18[e]	15% glass 3A 42.5% viscose 42.5% vinyon	3.7	--	16	96
E-18-30[f]	30% glass 3A 35% viscose 35% vinyon	2.0	--	16	99
E-18-35[f]	35% glass 3A 32.5% viscose 32.5% vinyon	1.0	--	31	95
57-SYN-3.5[f]	30% glass 3A 25% Dacron fibrid 10% Dacron 35% Dacron D-90	2.76	--	4	99
57-SYN-8[f]	same as 57-SYN-3.5	1.82	--	18	98
57-SYN-12[f]	same as 57-SYN-3.5	1.86	--	12	93
57-SYN-1-40[f]	same as 57-SYN-3.5	0.98	--	20	86
57-SYN-1-44[f]	same as 57-SYN-3.5	0.93	--	28	87
58-SYN-10[f]	35% glass 3A 25% Dacron fibrid 40% Dacron	1.87	--	10	97
58-SYN-33[f]	same as 58-SYN-10	0.99	--	22	93

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[a] Two layers.

[b] 36% Rhoplex B-15 binder.

[c] 7% binder.

[d] MIL-F-1378A, 30 November 1955.

[e] Edgewood Arsenal.

[f] Handsheets obtained from Hollingsworth and Vose Company.

Liner E-18 was a special U. S. Army paper with outstanding aeroso filtration properties, but its weight of 3.7 oz/yd^2 was greater than desirabl for use in a multi-layer garment.

Samples E-18-30 and E-18-35 were similar papers, and were supplied by Hollingsworth and Vose Company as handsheets. They contained a higher percentage of glass fiber and were lighter in weight than Liner E-18. Although weight was reduced substantially (3.7 to 1.0 oz/yd^2) and air permeability was almost doubled (18 to 31 ft^3/min/ft^2) by increasin the percentage of glass fiber from 15% to 35%, the aerosol retention was only slightly affected (reduced from 98% to 95%). However, the breaking strengths and tearing strengths of these glass-viscose-vinyon papers were lower than those of the papers containing glass, Dacron, and Dacron fibrids, which were also supplied by Hollingsworth and Vose as handsheets. These properties are tabulated in Table II-2.

The data indicate that a paper containing glass fibers, Dacron fibers, and Dacron fibrids (for example, 58-SYN-33) should have acceptable weight (1.0 oz/yd^2), air permeability (22 ft^3/min/ft^2), and aerosol retention (93%) for use as the middle layer.

C. Inner Layer

The function of the inner layer was to prevent the passage of agent vapor. To accomplish this objective, a woven Fortisan fabric and a rayon nonwoven web were treated with a combination of S-330 and Hycar 4501. The S-330 treating bath was prepared according to directions furnished by Edgewood Arsenal. The Fortisan fabric, of rip-stop construction and weighing 1.8 oz/yd^2, was supplied by the U. S. Army Natick Laboratories. The nonwoven rayon fabric was a 1.9-oz/yd^2 Narcon web. The evaluation of these materials consisted of determining whether the recommended amount (0.7 oz/yd^2) of the S-330 Hycar 4501 combination could be applied to the fabrics without too great a loss of air permeability.

Attempts to apply 0.7 oz/yd^2 of S-330 solids to the Fortisan fabric by padding were unsuccessful. However, it was possible to apply that amount by spraying one side of the fabric with the S-330 treating bath. After the sprayed fabric was dried and cured for 10 minutes at 150°C, it had a glazed surface and an air permeability of less than 1 ft^3/min/ft^2.

Table II-2. Strength of Papers Evaluated for Middle Layer

Paper[a]	Breaking strength, lb/in.	Elmendorf tear, g
Liner E-18	1.2[b]	41[c]
E-18-30	1.3	32
E-18-35	0.4	16
57-SYN-3.5	7.5	640
57-SYN-8	4.4	192
57-SYN-12	3.9	272
57-SYN-1-40	2.6	d
57-SYN-1-44	2.6	d
58-SYN-10	3.5	d
58-SYN-33	1.9	d

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[a] The fiber composition is given in Table II-1.

[b] Average of cross (0.92 lb/in.) and machine (1.57 lb/in.) direction values. The other papers have no machine direction.

[c] Average of cross (51 g) and machine (31 g) direction values.

[d] Insufficient sample available.

Another sample of the fabric sprayed to apply 0.24 oz/yd^2 had an air perm bility of 8 ft^3/min/ft^2. A sample of the same Fortisan fabric treated with S-330 by the U. S. Army Natick Laboratories had an average air permeability of 9 ft^3/min/ft^2 and an average total solids add-on of 0.30 oz/yd^2 (determined by weighing treated and untreated samples that were condition prior to weighing).

Several experiments were conducted to determine the effect of the method of treatment and the amount of solids on the air permeabilities of the Fortisan and the nonwoven rayon fabrics. Some samples were sprayed with the S-330 bath and slack dried at 150°C; others were placed on tenter frames prior to spraying and were kept on the frames while they were dried at 150°C (one sample was dried at 95°C). The results are shown in Table II-3. The air permeability of the Fortisan fabric was greatly decreased by a solids add-on of 0.5% or more, while the desired amount (0.65 oz/yd^2) was applied to the rayon nonwoven without a great reduction of its air permeability.

Table II-3. Effect of S-330 Treatment on the Air Permeability of Fabrics

Tension during treatment	Cure temperature, °C	Solids add-on, %	Air permeability, $ft^3/min/ft^2$, 0.5 in. water
A. $1.8\ oz/yd^2$ Fortisan			
-	-	None	50
Slack	150	0.70	< 1
Slack	150	0.24	8
Framed	150	0.51	1
Framed	150	0.23	44
Framed	95	0.35	40
B. $1.9\ oz/yd^2$ rayon (Narcon) nonwoven fabric			
-	-	None	455
Slack	150	0.14	400
Slack	150	0.65	360

IV. EVALUATION OF MATERIALS FOR A TWO-LAYER OVERGARMENT

Several two-layer systems were investigated with respect to their resistance to penetration by liquid agents, their air permeability, and their aerosol retention. In a two-layer system, the outer layer was expected to provide the primary resistance to penetration by liquids and to wear; the inner layer was expected to retard the passage of vapor. Both layers were expected to contribute to the retention of aerosols. The outer-layer materials studied were (see Section III-A):

Nylon-cotton fabric — cotton warp and nylon filling oxford, treated with Quarpel, and weighing 5.5 oz/yd^2

Experimental Paper 6-21-62R — nylon-reinforced 50:50 nylon-wood pulp paper impregnated with Rhoplex HA-12 and overtreated with FC-208

The inner-layer materials were (see Section III-C):

Fortisan fabric — weighing 1.8 oz/yd^2, with an add-on of 0.7 oz/yd^2 of S-330 and Hycar 4501 solids

Fortisan fabric — weighing 1.8 oz/yd^2, with an add-on of 0.24 oz/yd^2 of S-330 and Hycar 4501 solids

Table II-4 gives data for each material individually and also for two-layer composites of: (1) the oxford cloth and the Fortisan fabric with 0.7 oz/yd^2 of S-330; (2) the oxford cloth and the Fortisan fabric with 0.24 oz/yd^2 of S-330; and (3) the Experimental Paper 6-21-62R and the Fortisan fabric with 0.24 oz/yd^2 of S-330. The oxford cloth and the Experimental Paper 6-21-62R served as the top layer in the drop and expulsion tests with liquid agents. None of the three two-layer composites was penetrated by the liquid agents. The air permeability of the oxford cloth and of the composites containing it was less than 1 ft^3/min/ft^2, and the aerosol retention of these materials was relatively good. The paper-Fortisan composite had higher air permeability, but its aerosol retention was only 24%.

[illegible]

[redacted]

Material	Resistance to liquid CW agents						Air permeability, $ft^3/min/ft^2$, 0.5 in. water	Aerosol retention, %
	VX		GB		HD			
	Drop test[a]	Expulsion test[b]	Drop test[a]	Expulsion test[b]	Drop test[a]	Expulsion test[b]		
Oxford cloth	0/6	15/16	0/6	5/16	0/12	6/16	<1	66
Paper 6-21-62R	0/12	0/8	0/6	0/8	1/12	0/8	17	16
Fortisan fabric, 0.7 oz/yd^2 of S-330	5/6	8/8	6/6	2/8	6/6	7/8	<1	38
Fortisan fabric, 0.24 oz/yd^2 of S-330	6/6	8/8	6/6	8/8	6/6	8/8	11	27
Com[redacted]osite of oxford cloth and Fortisan fabr with 0.7 oz/y of S-330	0/6	0/8	0/6	0/8	0/6	0/8	<1	91
Com[redacted]osite of oxford cloth and Fortisan fabr with 0.24 oz/ of S-330	0/6	1/8	0/6	0/8	0/6	0/8	<1	63
Com[redacted]osite of paper 6-21 62R and Fort an fabric with 0.24 oz/yd^2 of S-330	0/6	0/8	0/6	0/8	0/6	0/8	10	24

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[a] Drops penetrated/drops tested, 7 to 8 mg drops.

[b] Specimens penetrated/specimens tested.

V. ONE-LAYER SYSTEM

Before the requirement for aerosol retention was dropped, some consideration was given to properties necessary in a single layer of mat that would protect against liquid, vapor, and particulate agents. It was visualized that a nonwoven fabric could be sprayed on one side with FC-2 to give resistance to liquid agents, and on the other side with a mixture o S-330 and Hycar 4501 to give resistance to the passage of gases. Becaus it was anticipated that resistance to penetration by aerosols would be controlled by the structure of the fabric, a theoretical study was made on the effects of the important filter parameters (fiber diameter, filter thicknes and bulk density) of nonwovens on filtration efficiency. Some experiment work was done on the effects of added binders in nonwoven fabrics on filtration efficiency. However, no single-layer material was evaluated experimentally for its resistance to penetration by agents in all three physical forms.

A. Effects of Filter Parameters on Aerosol Filtration Efficiency

Initially, it was thought that there were empirical equations that would allow the quantitative prediction of filtration efficiency from the measured parameters of the filtration system. However, a few calculatio with these equations, with data obtained from the literature on a filter who filtration efficiency had been experimentally determined, quickly showed poor correlation between the calculated values of filtration efficiency (abou 8%) and the experimentally determined values (about 32%). Therefore, the discussion to follow should be viewed as shedding insight only on the qualitative effect of filter parameters — even though the discussion is couched in quantitative terms.

The equations used for the calculations were those of Blasewitz and Judson.[1] Their equations were developed for performance in filtering 0.5-micron particles. Since we were interested in particles having an

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[1] A. G. Blasewitz and B. F. Judson, Chem. Engr. Progress 51, No. 1, page 6-J (January, 1955).

average diameter of 2.5 to 3.0 microns, the efficiencies calculated by the Blasewitz equations were altered to account for the difference in particle size according to the charts of Stern, Zeller, and Schekman.[2]

1. Fiber diameter

The Blasewitz equations were used to calculate filtration efficiencies. The filter assumed for the calculations had the following characteristics:

Thickness - 0.004 in.

Weight per square yard - 3 oz (62.5 lb/ft^3)

Fiber diameter - varied

The calculated efficiencies for 0.5-micron particles are plotted as the dotted line in Figure II-1. Efficiencies for 2.5-micron particles as estimated from the Stern-Zeller charts are shown as the solid lines. Note that if the diameter of the fibers exceeds about 1.5 microns, the filtration efficiency decreases rapidly.

2. Mat thickness

The filter assumed for these calculations had the following characteristics:

Weight per square yard - 3 oz

Fiber diameter - 1.3 microns

Thickness - varied

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[2] S. C. Stern, H. W. Zeller, and A. I. Schekman, J. Colloid Sci. 15, 546 (1960).

[redacted]

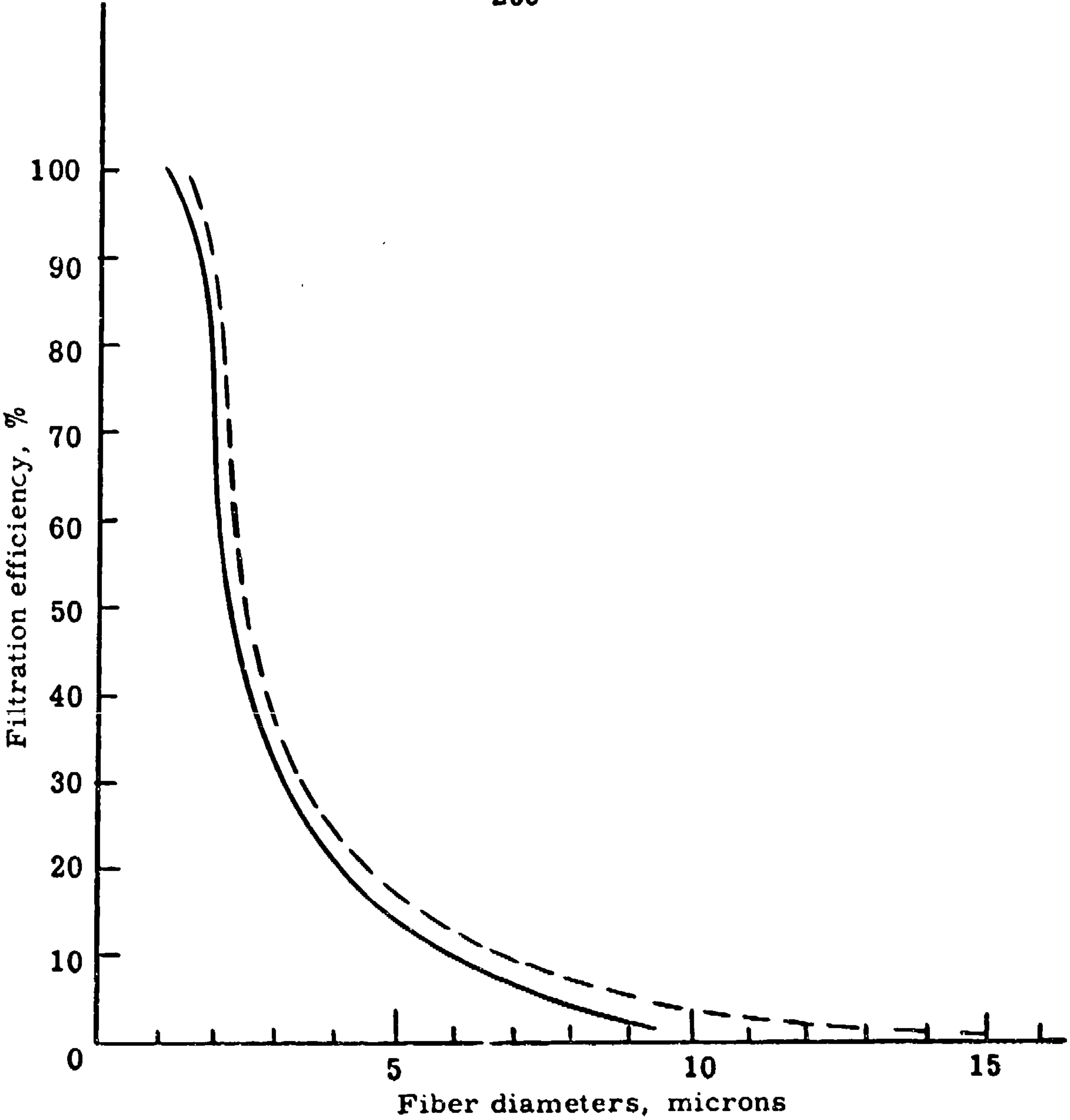

Figure II-1. Effect of Fiber Diameter on Filtration Efficiency

[redacted]

Calculations based on the variation in thickness with a constant weight of 3 oz/yd^2 indicated that the filtration efficiency was a minimum at a thickness of about 0.03 in. As the thickness increased, the bulk density decreased, which made the filter more porous and less efficient. However, the increase in thickness (i.e. the number of layers of fibers) tended to make the filter more efficient, and, at thicknesses greater than 0.03 in., the increase in efficiency because of increased thickness more than offset the decrease in efficiency because of decreased bulk density. The minimum efficiency was calculated to be 99% at 0.03 in.

3. Bulk density

The filter assumed for these calculations had the following properties:

Fiber diameter - 1.3 microns

Thickness - 0.004 in.

Weight per square yard - varied

The variation in filtration efficiency with bulk density is shown in Figure II-2, with the bulk density expressed as weight per square yard for a 0.004 in. thickness of mat. In Figure II-2, it can be seen that at 2 oz/yd^2, the filtration efficiency is 99.9%, and even at 1 oz/yd^2, the efficiency is 90.5%, when 1.3 micron glass fibers are used.

4. Discussion

If it is assumed that a 1.5-oz/yd^2 filter mat is used as the filtering medium, a three-layer construction might be developed in which the total weight of the treated outer and inner layers could be 2.5 oz/yd^2. Alternatively, a nonwoven construction might be used in which 1.5 oz/yd^2 of 1.3-micron glass fibers are interspersed with larger fibers to add strength, if the treatments used to bind the nonwoven material or to effect vapor and liquid impenetrability do not adversely affect the filtration performance.

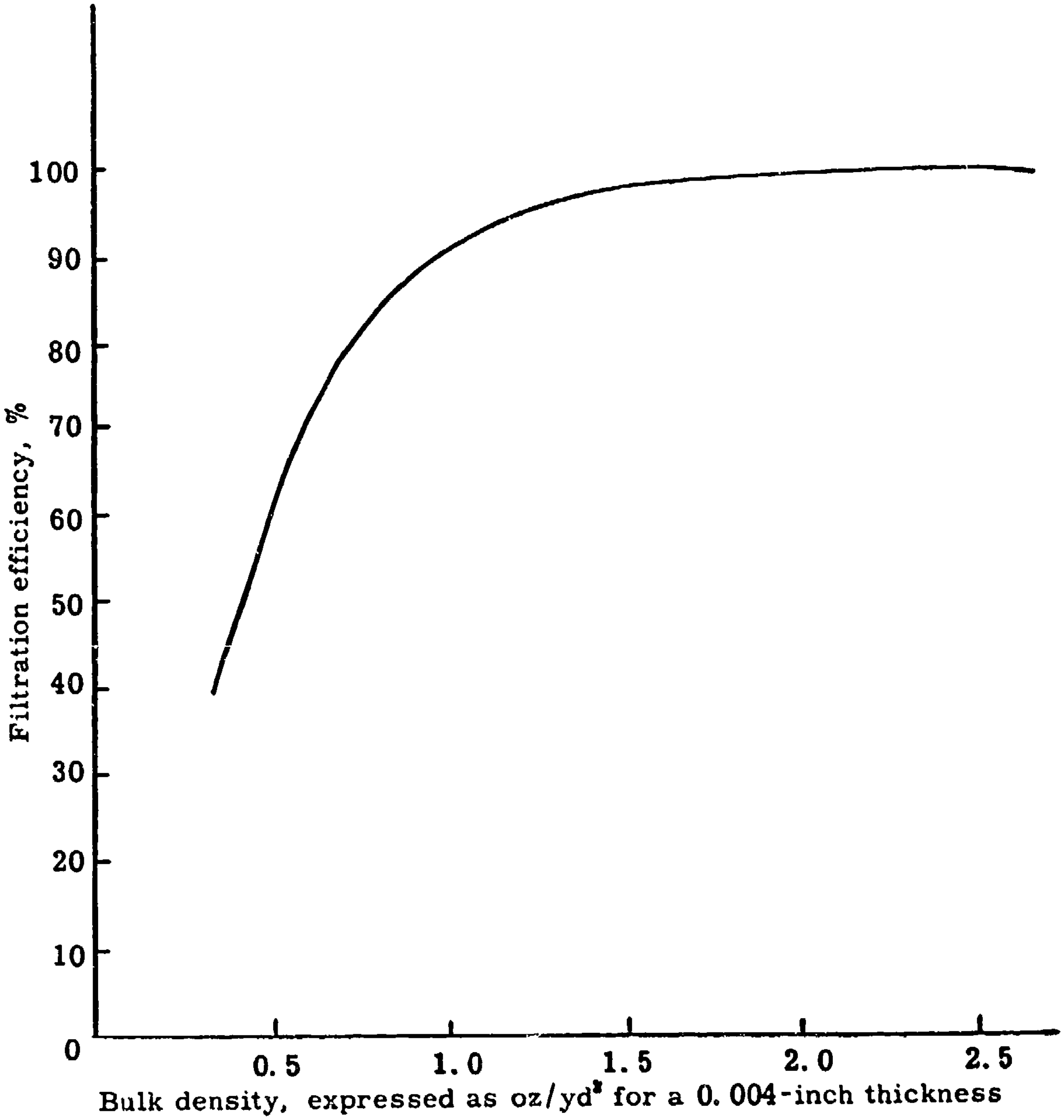

Figure II-2. Effect of Bulk Density on Filtration Efficiency

[redacted]

B. Effects of Binders on Aerosol Filtration Efficiency

As is shown in the discussion above, micro-diameter fibers are necessary in a nonwoven fabric or paper to provide acceptable aerosol retention. Retentive filters usually contain a mixture of micro-diameter fibers and other fibers of paper-making quality. Both glass and asbestos have been used in aerosol filters as the small-diameter fiber. It was thought possible that the effective diameters of the micro-fibers might be increased by the binders that are necessary to provide the strength needed in a paper or nonwoven fabric for garment applications. Therefore, several experiments were made to determine the effects of binders on the retentivity of a filter material.

Samples of the material designated as Liner E-18 (Section III-B) were treated with Rhoplex B-15 and with a S-330-Hycar 4501 combination. Attempts to apply the treatments by padding were unsuccessful; therefore, they were applied by spraying the Rhoplex B-15 on one side and the S-330-Hycar 4501 on the other. Table II-5 shows that the amounts of solids added in these experiments did not appreciably affect the aerosol retention and only slightly decreased the air permeability. These results substantiate the hypothesis that a nonwoven fabric or paper having resistance to liquid, aerosol, and vapor CW agents can be developed.

[redacted]

Table II-5. Effects of Binders on the Air Permeability and Aerosol Retention of Liner E-18

Sample treatment	Solids add-on, %	Air permeability, $ft^3/min/ft^2$, 0.5 in. water	Aerosol retention, %
None	0	18	98
Rhoplex B-15	25	16	96
Rhoplex B-15	50	10	98
S-330 and Hycar 4501	19[a]	16	95

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[a] 0.7 oz/yd^2.

PART III. DEVELOPMENT OF MATERIALS FOR AN OVERGARMENT PROVIDING PROTECTION AGAINST LIQUID AND VAPOR

I. INTRODUCTION

Part II of this report describes the development of materials for an overgarment intended to be durable enough for wear for three to twenty-one days and to provide protection against CW agents in liquid, vapor, and aerosol forms for a minimum of six hours during this period. During the course of this work, the requirement for protection against aerosols was dropped. Therefore the work that is described in Part III was concerned only with materials to provide liquid and vapor protection. Much of the data in Parts I and II of this report was used in the work described in Part III.

Materials for two types of overgarments were studied. Materials were investigated for use in a garment in which a single layer of fabric was treated with repellent to prevent the passage of liquids and also with a reactive compound to prevent the passage of vapors. Other studies were concerned with a two-layer material in which the outer layer was treated with a repellent and the inner layer with a reactive or adsorptive compound. Properties of each of the two layers were determined, and properties of composites of the two layers were also determined.

[redacted]

II. SUMMARY

On the basis of data on air permeability, resistance to penetration by liquid VX, and resistance to penetration by HD vapor, it was concluded that one-layer systems were less satisfactory than two-layer systems for protection against CW agents in liquid and vapor forms. This conclusion was reached after studying 33 fabrics, mostly cottons, each with two or more different treatments consisting of FC-208 or Quarpel for repellency and S-330 plus Hycar 4501 or Hycar 2671 for resistance to penetration by vapor.

Forty-one fabrics, mostly cotton, were treated with Zepel B or FC-208 and evaluated for use as outer layers of two-layer systems. Treated fabrics having a cover factor greater than 40 or a density greater than $0.35\ \mathrm{oz/in}^3$ were not penetrated by liquid VX. Resistance to penetration by liquid VX in the expulsion test increased with increasing fabric thickness, but the relationship was not linear. Resistance to liquid VX also increased with decreasing air permeability of the fabric. Double layers of the treated fabrics were completely resistant to penetration by liquid VX.

In the expulsion test with VX, fabrics treated with Zepel B were superior to those treated with FC-208. Fabrics treated with Zepel B were also more resistant to weathering.

Mercerization of cotton fabrics before treatment with FC-208 improved their resistance to penetration by liquid VX. A significant improvement was obtained when the mercerized fabric was dried under controlled tension to produce 5% shrinkage. Mercerization resulted in an increase in weight of the treated fabric and a reduction of about 50% in the air permeability.

A pressure-sensitive, fiber-reinforced plastic tape (3M No. 880) had adequate adhesive strength and resistance to penetration by liquid VX, and appeared to be suitable for the repair of the torn outer-layer fabrics.

For the inner layer of two-layer systems, a 1.8-oz/yd^2 Fortisan fabric, treated with S-330 and Hycar 2671, had some desirable characteristics, but its air permeability and water-vapor transmission rate were low. Varying the method of application of the S-330 and the Hycar 2671 did not yield sufficient improvement in these properties.

[redacted]

[redacted]

Rayon nonwoven fabrics for the inner layer had lower strengths and higher air permeabilities than woven fabrics. Rayon nonwoven fabrics treated separately with S-330 and Hycar 2671 were more resistant to penetration by HD vapor than the same fabrics treated with a single-bath mixture of S-330 and Hycar 2671. Hycar 2671 and Hycar 4501 were the best of several binders evaluated with S-330 for protection against HD vapor. A rayon nonwoven fabric treated with a mixture of carbon and Hycar 2671 had excellent resistance to penetration by HD vapor.

Thirty-six two-layer systems having an outer layer of a 6.5-oz/yd^2 mercerized cotton fabric treated with Zepel B and various materials as inner layers were evaluated. The weights of these two-layer systems ranged from 8.6 oz/yd^2 to 13.3 oz/yd^2. The air permeabilities of the two-layer systems with a treated-Fortisan-fabric inner layer ranged from 0.5 to 3 ft^3/min/ft^2; with a rayon-nonwoven-fabric inner layer the range was 13 to 17 ft^3/min/ft^2; and with a polyurethane foam/nylon fabric laminate inner layer it was 14 to 17.5 ft^3/min/ft^2. All of the two-layer systems were considered to have satisfactory resistance to penetration by liquid VX. Satisfactory resistance to penetration by HD vapor ($<5\%$ penetration) was obtained with systems having Fortisan- or rayon-nonwoven-fabric inner layers containing 0.5 oz/yd^2 of carbon, and with foam/fabric inner layers containing 1.0 oz/yd^2 of carbon. With an S-330-treated inner layer, only the systems with a foam/fabric laminate gave satisfactory resistance to HD vapor; systems with Hycar 4501 as a binder for the S-330 in the inner layer had better resistance than systems without a binder. With a CC-2 treated inner layer, a rayon nonwoven fabric and a foam/fabric laminate had satisfactory resistance to penetration by HD vapor; the use of Hycar 4501 with CC-2 decreased the resistance of the systems with foam/fabric inner layers, increased that of systems with a Fortisan inner layer from an unsatisfactory level to a satisfactory level, and had no apparent effect in systems with a rayon nonwoven fabric. The resistance of most of the two-layer systems to penetration by vapor from a drop of liquid HD was only slightly better than or not significantly different from the resistance of the outer layer alone. Systems with inner layers containing carbon and Hycar 4501 gave better protection against the vapors from drops of liquid VX or liquid GB than did systems with other inner-layer treatments.

[redacted]

Accelerated aging at 80°C and 100% relative humidity caused severe degradation in two-layer systems with S-330 in the inner layer. A foam/fabric inner-layer system with carbon/Hycar 4501 treatment and rayon-nonwoven-fabric inner-layer system with CC-2/Hycar 4501 treatment were significantly less resistant to HD vapor after aging. The HD-vapor resistance of several other two-layer systems was not affected.

Exposure to body perspiration did not affect the resistance to HD vapor penetration of a rayon nonwoven fabric treated with carbon and Hycar 4501 or of a polyurethane foam/nylon fabric laminate treated similarly.

A comparison of several binders for use in a rayon-nonwoven-fabric inner layer treated with carbon indicated that little difference existed with respect to physical properties or to resistance to penetration by HD vapor. However, fabrics treated with Hycar 2600X83 were somewhat less stiff than fabrics treated with Hycar 4501, Rhoplex HA-8, or Rhoplex B-15 and, therefore, Hycar 2600X83 was used in subsequent plant production of materials.

On the basis of the laboratory evaluations, it was concluded that a rayon nonwoven fabric and a polyurethane foam/nylon fabric laminate, each treated with a carbon-latex mixture, offered the best possibilities for the inner layer of a two-layer system. Therefore, plant production of materials of these types was undertaken and substantial quantities were supplied to U. S. Army Natick Laboratories for further evaluation.

III. EVALUATION OF ONE-LAYER MATERIALS

The fabrics evaluated for use as single layers were woven fabrics of various weights, weaves, and constructions. Most of them were cottons, chosen partly because of cost considerations. Detailed descriptions of these fabrics are given in the Appendix.

The repellent materials used were FC-208 and Quarpel. The Quarpel-treated fabrics were supplied by the U. S. Army Natick Laboratories. The FC-208 was applied by padding or by spraying. Mixtures of S-330 and either Hycar 4501 or Hycar 2671 and a mixture of activated carbon and natural rubber latex were used to provide vapor protection. The S-330/Hycar mixtures were usually applied by spraying, and the carbon/natural rubber mixture was applied by brushing. The amounts of these mixtures applied and the procedures for preparation of the treating baths were those recommended by the U. S. Army Chemical Research and Development Laboratories.

Table III-1 lists the types of fabrics, the types of treatments, the weights of the treated fabrics, the air permeabilities of the treated fabrics, and the resistances to penetration by liquid agents as shown by drop tests and expulsion tests; and Table III-2 gives the resistances to penetration by HD vapor of 22 of the treated fabrics. In the columns headed "Fabric-treatment No.," the first digit identifies the fabric and the second digit identifies the treatment given to that fabric.

It was concluded from these studies that one-layer systems were not as promising for use in overgarments to provide protection against liquid and gaseous CW agents as multi-layer systems.

[redacted]

Table III-1. Treatment and Evaluation of Materials for One-Layer Systems

Fabric-treatment No.	Fabric	Weight, oz/yd^2	Treatment (% solids applied)	Weight of treated fabric, oz/yd^2	Air permeability, ft^3/min/ft^2, 0.5 in. water	Penetration by liquid agents^{a,b}				
						Drop test			Expulsion test	
						VX	GB	HD	VX	GB
1-1	Nylon-cotton oxford	5.0	4-6% Quarpel; 0.19 oz/yd^c S-330/Hycar 4501 sprayed on one side	5.3	<1	-	-	-	0/8	-
1-2	Nylon-cotton oxford	5.0	4-6% Quarpel; 0.25 oz/yd^c S-330/Hycar 4501 sprayed on one side	5.4	<1	-	-	-	0/8	-
1-3	Nylon-cotton oxford	5.0	4-6% Quarpel; 0.42 oz/yd^2 S-330/Hycar 4501 sprayed on one side	5.6	<1	-	-	-	0/8	-
1-4	Nylon-cotton oxford	5.0	4-6% Quarpel; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on one side	5.8	<1	-	-	-	0/8	-
1-5	Nylon-cotton oxford	5.0	0.7 oz/yd^2 S-330/Hycar 4501 sprayed on one side first, 4% FC-208 sprayed on other side	5.8	<1	-	-	-	0/8	-
1-6	Nylon-cotton oxford	5.0	4% FC-208 sprayed on one side first; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	5.8	<1	-	-	-	0/8	-
1-7	Nylon-cotton oxford	5.0	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	6.6	<1	5/6	0/6	-	0/8	0/8
1-8	Nylon-cotton oxford	5.0	4% FC-208 padded; 1.4 oz/yd^2 carbon/natural rubber mixture brushed	7.2		0/6	0/6	0/6	0/8	0/8
2-1	Nylon oxford	4.4	4-6% Quarpel; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	5.3	<1	-	-	-	0/8	-
2-2	Nylon oxford	4.4	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	5.6	<1	-	-	-	0/8	-
3-1	Textured nylon	4.6	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	5.8	8	-	-	-	3/8	-
3-2	Textured nylon	4.6	4% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	6.0	7	-	-	-	7/8	-
4-1	Cotton chintz	3.2	4% FC-208 padded; 0.7 oz/yd^2 + S-330/Hycar 4501 sprayed	4.5	7	-	-	-	8/8	-
5-1	Cotton lawn	3.1	4% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	4.4	5	-	-	-	8/8	-
5-2	Cotton lawn	3.1	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	4.5	6	-	-	-	8/8	-
5-3	Cotton lawn	3.1	8% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	4.7	3	-	-	-	7/8	-
6-1	Cotton print cloth	3.3	4% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	-	49	-	-	-	8/8	-
6-2	Cotton print cloth	3.3	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	5.0	13	-	-	-	8/8	-
6-3	Cotton print cloth	3.3	8% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	-	49	-	-	-	6/8	-
6-4	Cotton print cloth	3.3	8% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	4.9	13	-	-	-	7/8	-
7-1	Cotton sateen	8.0	4% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	10.3	12	-	-	-	1/8	-
7-2	Cotton sateen		8% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	10.7	6	-	-	-	0/8	-

Table III-1 (continued). Treatment and Evaluation of Materials for One-Layer Systems

Fabric-treatment No.	Fabric	Weight, oz/yd^2	Treatment (% solids applied)	Weight of treated fabric, oz/yd^2	Air permeability, ft^3/min/ft^2, 0.5 in. water	Penetration by liquid agents^{a,b} Drop test VX	Drop test GB	Drop test HD	Expulsion test VX	Expulsion test GB	Expulsion test HD
8-1	Cotton poplin	5.5	4% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	7.0	<1	-	-	-	1/8	-	-
8-2	Cotton poplin	5.5	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	7.3	2	6/6	0/6	-	0/8	0/8	-
8-3	Cotton poplin	5.5	4% FC-208 padded; 1.4 oz/yd^2 carbon/natural rubber mixture brushed	9.2	<1	2/6	0/6	0/6	0/8	1/8	0/8
9-1	Pima cotton broadcloth	3.0	4% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed on other side	4.4	<1	-	-	-	8/8	-	-
10-1	Cotton broadcloth	3.5	4% FC-208 sprayed on one side; 0.7 oz/yd^2 S-330 Hycar 4501 sprayed on other side	4.9	20	-	-	-	8/8	-	-
10-2	Cotton broadcloth	3.5	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501	4.7	22	3/6	0/6	-	7/8	8/8	-
10-3	Cotton broadcloth	3.5	4% FC-208 padded; 0.7 oz/yd^2 carbon/natural rubber mixture brushed	5.1	<1	1/6	0/6	0/6	7/8	8/8	-
11-1	Cotton sheeting	7.0	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 4501 sprayed	9.4	48	0/6	0/6	-	1/8	0/8	-
11-2	Cotton sheeting	7.0	4% FC-208 padded; 1.4 oz/yd^2 carbon/natural rubber mixture brushed	10.2	<1	0/6	0/6	0/6	1/8	0/8	0/8
12-1	Cotton sheeting	4.5	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	5.6	20	6/6	-	-	0/8	-	-
12-2	Cotton sheeting	4.5	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 2671 sprayed	5.6	13	0/6	-	-	2/8	-	-
13-1	Cotton sheeting	4.0	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	4.6	49	0/6	-	-	5/8	-	-
13-2	Cotton sheeting	4.0	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 2671 sprayed	5.0	39	0/6	-	-	3/8	-	-
14-1	Cotton sheeting 405	5.3	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	5.6	31	0/6	-	-	8/8	-	-
14-2	Cotton sheeting	5.3	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 2671 sprayed	6.5	16	0/6	-	-	6/8	-	-
15-1	Cotton Osnaburg	7.6	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	8.0	34	0/6	-	-	2/8	-	-
15-2	Cotton Osnaburg	7.6	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 2671 sprayed	8.8	30	0/6	-	-	0/8	-	-
16-1	Cotton May Duck 185	6.4	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	7.0	9	0/6	-	-	8/8	-	-
16-2	Cotton May Duck	6.4	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 2671 sprayed	7.5	30	0/6	-	-	6/8	-	-
17-1	Cotton oxford	8.8	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	10.3	<1	0/3	-	-	0/8	-	-
17-2	Cotton oxford	8.8	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 2671 sprayed	10.3	<1	0/6	-	-	0/8	-	-
18-1	Cotton oxford	6.2	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	7.2	<1	0/6	-	-	0/8	-	-
18-2	Cotton oxford	6.2	4% FC-208 padded; 0.7 oz/yd^2 S-330/Hycar 2671 sprayed	7.4	<1	0/6	-	-	0/8	-	-
19-1	Cotton oxford	11.5	0.7 oz/yd^2 S-330/Hycar 2671 padded; 4% FC-208 overpadded	12.7	<1	0/6	-	-	0/8	-	-

Table III-1 (continued). Treatment and Evaluation of Materials for One-Layer Systems

Fabric-treatment No.	Fabric	Weight, oz/yd²	Treatment (% solids applied)	Weight of treated fabric, oz/yd²	Air permeability, ft³/min/ft², 0.5 in. water	Penetration by liquid agent			
						Drop test			[illegible]
						VX	GD	HD	VX
19-2	Cotton oxford	11.5	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	13.3	<1	0/8	-	-	0/8
20-1	Cotton oxford	6.8	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	7.9	<1	0/6	-	-	0/8
20-2	Cotton oxford	6.8	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	8.1	<1	0/6	-	-	0/8
21-1	Cotton oxford	12.3	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	13.7	<1	0/6	-	-	0/8
21-2	Cotton oxford	12.3	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	14.2	<1	0/6	-	-	0/8
22-1	Cotton oxford	11.2	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	12.7	<1	0/6	-	-	0/8
22-2	Cotton oxford	11.2	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	12.8	<1	0/6	-	-	0/8
23-1	Cotton oxford	6.3	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	7.8	<1	0/6	-	-	0/8
23-2	Cotton oxford	6.6	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	7.9	<1	0/6	-	-	0/8
24-1	Cotton oxford	12.0	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	13.3	<1	0/6	-	-	0/8
24-2	Cotton oxford	12.0	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	13.6	<1	0/6	-	-	0/8
25-1	Cotton oxford	6.4	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	7.4	<1	0/6	-	-	0/8
25-2	Cotton oxford	6.4	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	7.6	<1	0/6	-	-	0/8
26-1	Cotton oxford	11.4	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	13.5	<1	0/6	-	-	0/8
26-2	Cotton oxford	11.4	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	13.4	<1	0/6	-	-	0/8
27-1	Cotton oxford	7.3	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	8.3	<1	0/6	-	-	0/8
27-2	Cotton oxford	-	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	8.8	<1	0/6	-	-	0/8
28-1	Duck DF	7.5	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	8.7	8	0/6	-	-	0/8
28-2	Duck DF	7.5	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	9.0	8	0/6	-	-	0/8
29-1	Cotton sateen	8.5	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	9.2	8	0/6	-	-	0/8
29-2	Cotton sateen	8.5	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	9.3	10	0/6	-	-	0/8
30-1	Cotton twill	8.4	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	9.2	7	0/6	-	-	3/8
30-2	Cotton twill	8.4	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	9.7	6	0/6	-	-	0/8
31-1	Cotton drill	7.1	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	8.0	9	0/6	-	-	0/8
31-2	Cotton drill	7.1	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	8.1	11	0/6	-	-	0/8
32-1	Cotton denim	7.4	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	7.6	80	0/6	-	-	3/8
32-2	Cotton denim	7.4	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	7.8	68	0/6	-	-	8/8
33-1	Cotton ticking	8.8	0.7 oz/yd² S-330/Hycar 2671 padded; 4% FC-208 overpadded	9.9	<1	0/6	-	-	0/8
33-2	Cotton ticking	8.8	4% FC-208 padded; 0.7 oz/yd² S-330/Hycar 2671 sprayed	10.4	1.5	0/6	-	-	0/8

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[a] Drops penetrated/drops tested.

[b] Fabrics 1 through 10 (except 1-7, 1-8, 10-2, and 10-3) were tested with 7 to 8 mg drops. All other tests were made with 3 to 4 mg drops.

Table III-2. Penetration of One-Layer Materials by HD Vapor[a]

Fabric-treatment[b] No.	Fabric	HD vapor concentration, µg/l		HD vapor penetration, µg/cm²		HD vapor retention,[c] %	
		0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
12-1	Cotton sheeting	29.1	29.2	17	61	51.3	14.9
13-1	Cotton sheeting	24.9	27.7	12	53	59.9	20.3
14-1	Cotton sheeting 405	24.9	27.7	11	49	63.2	26.3
15-1	Cotton Osnaburg	23.8	23.7	7	30	75.4	47.2
16-1	Cotton May Duck 185	23.8	23.7	13	46	54.5	19.2
17-1	Cotton oxford	29.1	29.2	17	60	51.3	14.4
18-1	Cotton oxford	29.1	29.2	15	53	57.0	38.6
19-1	Cotton oxford	29.1	29.2	10	37	71.3	47.2
20-1	Cotton oxford	29.1	29.2	15	52	57.0	25.8
21-1	Cotton oxford	29.1	29.2	10	48	71.3	31.5
22-1	Cotton oxford	29.1	29.2	9	37	74.2	47.2
23-1	Cotton oxford	27.0	35.5	16	67	50.6	21.4
24-1	Cotton oxford	27.0	35.5	12	56	63.0	34.2
25-1	Cotton oxford	27.0	35.5	15	53	53.7	37.8
26-1	Cotton oxford	27.0	35.5	9	29	72.2	66.0
27-1	Cotton oxford	27.0	35.5	14	66	56.8	22.5
28-1	Duck, DF	21.8	20.0	8.5	12.0	67.0	75.3
29-1	Cotton sateen	21.8	20.0	4.0	12.9	84.7	73.4
30-1	Cotton twill	21.8	20.0	6.8	28.3	74.0	41.7
31-1	Cotton drill	21.8	20.0	7.1	25.7	72.9	47.2
32-1	Cotton denim	21.8	20.0	11.8	41.1	55.0	15.3
33-1	Cotton ticking	21.8	20.0	5.8	12.6	77.9	74.0
12-2	Cotton sheeting	27.0	35.5	16	71	50.6	16.7
13-2	Cotton sheeting	29.1	29.2	18	64	48.4	8.7
14-2	Cotton sheeting 405	24.9	27.7	11	41	63.2	38.3
15-2	Cotton Osnaburg	23.8	23.7	14	49	51.0	13.8
16-2	Cotton May Duck 185	24.9	27.7	17	58	43.1	12.8
17-2	Cotton oxford	24.9	27.7	12	48	59.9	26.3
18-2	Cotton oxford	24.9	27.7	12	55	59.9	17.2
19-2	Cotton oxford	24.9	27.7	9	43	69.9	35.3
20-2	Cotton oxford	25.9	28.7	15	55	51.8	20.2
21-2	Cotton oxford	25.9	28.7	11	51	64.6	26.0
23-2	Cotton oxford	25.9	28.7	13	50	58.2	27.4
24-2	Cotton oxford	25.9	28.7	12	54	61.4	21.6
25-2	Cotton oxford	25.9	28.7	13	60	58.2	12.9
26-2	Cotton oxford	25.9	28.7	11	60	64.6	12.9
27-2	Cotton oxford	25.9	28.7	12	51	61.4	26.0
28-2	Duck, DF	21.8	20.0	8.9	34.0	66.0	29.9
30-2	Cotton twill	21.8	20.0	12.0	41.8	54.2	13.8
31-2	Cotton drill	21.8	20.0	6.2	20.0	76.3	58.8
32-2	Cotton denim	21.8	20.0	10.9	36.6	58.4	26.6
33-2	Cotton ticking	21.8	20.0	13.7	33.3	47.7	31.3

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[a] These measurements were made by the U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal.

[b] See Table III-1 for treatments applied.

[c]
$$\% \text{ retention} = 100 - \left[\frac{\text{penetration in } \mu g/cm^2}{\mu g/l \times 0.6 \ l/hr/cm^2 \times hr} \times 100 \right]$$

[redacted]

IV. EVALUATION OF MATERIALS FOR A TWO-LAYER GARMENT

The outer layer of a durable two-layer garment was required to provide the strength necessary for wear and to retard penetration by liquid agents. Because of the strength requirement, the fabrics selected for evaluation as an outer-layer material were all woven materials, mostly cottons, treated with a repellent. The inner-layer material, whose function was to retard agent vapor, was a nonwoven fabric, woven fabric, or foam treated with a reactive or adsorptive substance.

A. Outer-Layer Materials

1. Agent-repellent treatment of woven cotton fabrics

Forty-one fabrics, all but two of which were cottons, were evaluated specifically as outer-layer materials. These fabrics were treated with FC-208 or Zepel B to provide repellency toward liquid agents. Data were obtained on the air permeability and resistance to penetration by liquid VX in the drop and expulsion tests of each fabric. These data are summarized in Table III-3.

The data in Table III-3 were used to examine the relationships between expulsion-test results and properties of the treated fabrics. Figure III-1 indicates the relationship between the overall cover factor* (the sum of warp and filling cover factors) and penetration; treated fabrics having a cover factor above about 40 were not penetrated by liquid VX. Fabric density, which varies inversely with thickness and directly with cover factor when other variables are constant, was related to penetration by the curve of Figure III-2; fabrics with a density greater than about 0.35 oz/in.^{3} had good resistance to liquid VX. There was a general increase in resistance to penetration with increasing fabric thickness, but the expulsion-test data did not show the linear relationship that might

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* The cover factor is a measure of the amount of area covered by the yarns, and is calculated from $K = t/\sqrt{N}$, where K = cover factor, t = yarns/in., and N = cotton number.

[redacted]

Table III-3. Physical Properties and Resistance to VX Penetration of Woven Fabrics for Outer Layer

Fabric	Thickness of untreated fabric, mils	Weight, oz/yd²		Air permeability, $ft^3/min/ft^2$, 0.5 in. water		Penetration by VX[a]	
		Untreated fabric	Treated fabric	Untreated fabric	Treated fabric	Drop test	Expulsion test
A. Fabrics padded to apply 4.0% FC-208							
Cotton broadcloth	7.5	3.0	-	-	27	-	8/8[b]
Cotton lawn	7.8	3.1	3.6	53	32	1/6[b]	8/8[b]
Cotton chintz	5.4	3.2	3.5	18	25	0/6[b]	8/8[b]
Cotton print cloth	8.6	3.3	3.6	80	48	0/6[b]	8/8[b]
Cotton broadcloth	10.4	3.5	4.0	55	46	-	8/8[b]
Nylon oxford	9.1	4.4	-	-	< 1	-	1/8[b]
Nylon twill	13.2	4.6	-	-	19	-	4/8[b]
Nylon-cotton oxford	9.1	5.0	-	< 1	< 1	-	1/8[b]
Cotton poplin	11.4	5.5	5.8	6	3	0/6[b]	1/8[b]
Cotton sateen	20.3	8.0	8.6	18	18	0/6[b]	2/8[b]
Cotton oxford	-	5.2	5.4	22	21	3/6	8/8
Cotton sheeting	12.1	4.5	4.9	57	24	0/6	3/8
Cotton sheeting	12.0	4.0	4.2	134	58	0/6	7/8
Cotton sheeting 405	14.1	5.3	5.7	39	36	0/6	6/8
Cotton Osnaburg	22.5	7.6	8.1	39	40	0/6	2/8
Cotton May Duck	16.2	6.4	7.0	31	27	0/6	3/8
Cotton oxford	16.0	8.8	9.7	1.8	< 1	0/6	0/8
Cotton oxford	13.0	6.2	6.8	2.5	< 1	0/6	0/8
Cotton oxford	22.0	11.5	12.8	1.4	< 1	0/3	0/8
Cotton oxford	15.0	6.8	7.6	2.4	< 1	0/6	0/8
Cotton oxford	24.0	12.3	13.6	1.6	< 1	0/6	0/8
Cotton oxford	15.0	11.2	12.3	2.0	< 1	0/6	0/8
Cotton oxford	13.0	6.6	7.4	4.0	< 1	0/6	0/8
Cotton oxford	23.0	12.0	12.9	1.8	< 1	0/6	0/8
Cotton oxford	13.0	6.4	7.1	2.2	< 1	0/6	0/8
Cotton oxford	23.0	11.4	13.0	1.7	< 1	0/6	0/8
Cotton oxford	14.0	7.3	8.0	2.3	< 1	0/6	0/8
Duck, DF	21.0	7.5	8.4	45	10	0/6	1/8
Cotton sateen	21.0	8.5	-	19	-	0/6	0/8
Cotton twill	16.0	8.4	8.9	11	8	0/6	1/8
Cotton drill	19.0	7.1	7.4	32	11	0/6	0/8
Cotton denim	21.0	7.4	7.2	100	99	0/6	0/8
Cotton ticking	17.0	8.8	9.5	2.5	1	0/6	0/8
Cotton balloon cloth	-	2.5	2.6	93	35	-	8/8
Pima cotton broadcloth	-	3.0	3.2	36	27	-	8/8
B. Fabrics padded to apply 5% Zepel B							
Cotton lawn	7.8	3.1	3.6	53	27	-	8/8
Cotton balloon cloth	-	2.5	2.6	93	23	-	8/8
Cotton sateen	20.3	8.0	8.4	18	12	-	1/8
Pima cotton broadcloth	-	3.0	3.2	36	26	-	3/8
Cotton print cloth	8.6	3.3	3.4	80	38	0/6	6/8
Cotton poplin	11.4	5.5	5.7	6	2	0/6	0/8

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[a] Specimens or drops penetrated/specimens or drops tested.

[b] Drop size was 7 to 8 mg. Drop size was 3 to 4 mg in all other tests.

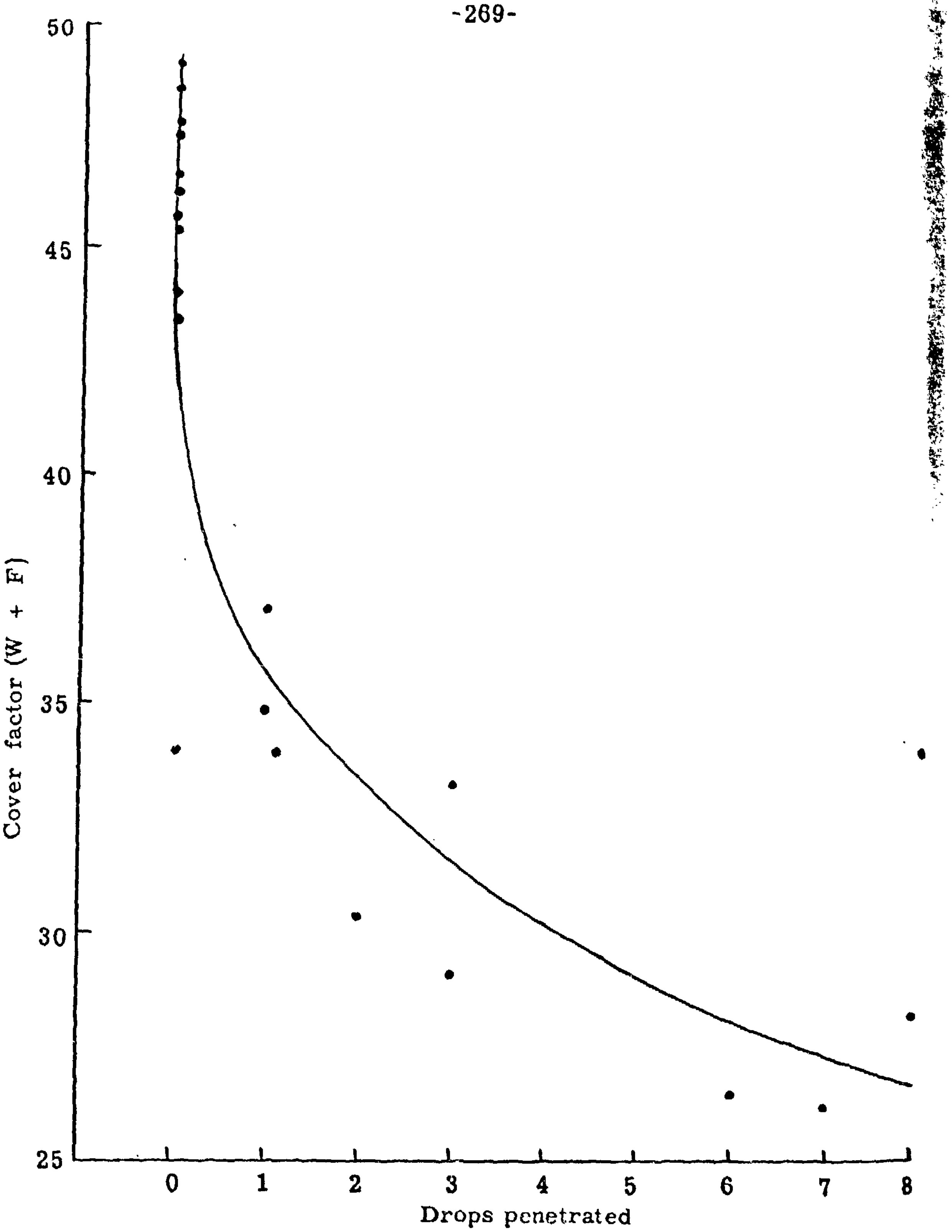

Figure III-1. Relationship Between Cover Factor (W + F) and Penetration (Expulsion) by VX Agent of Fabrics Treated with 4% FC-208 Solids

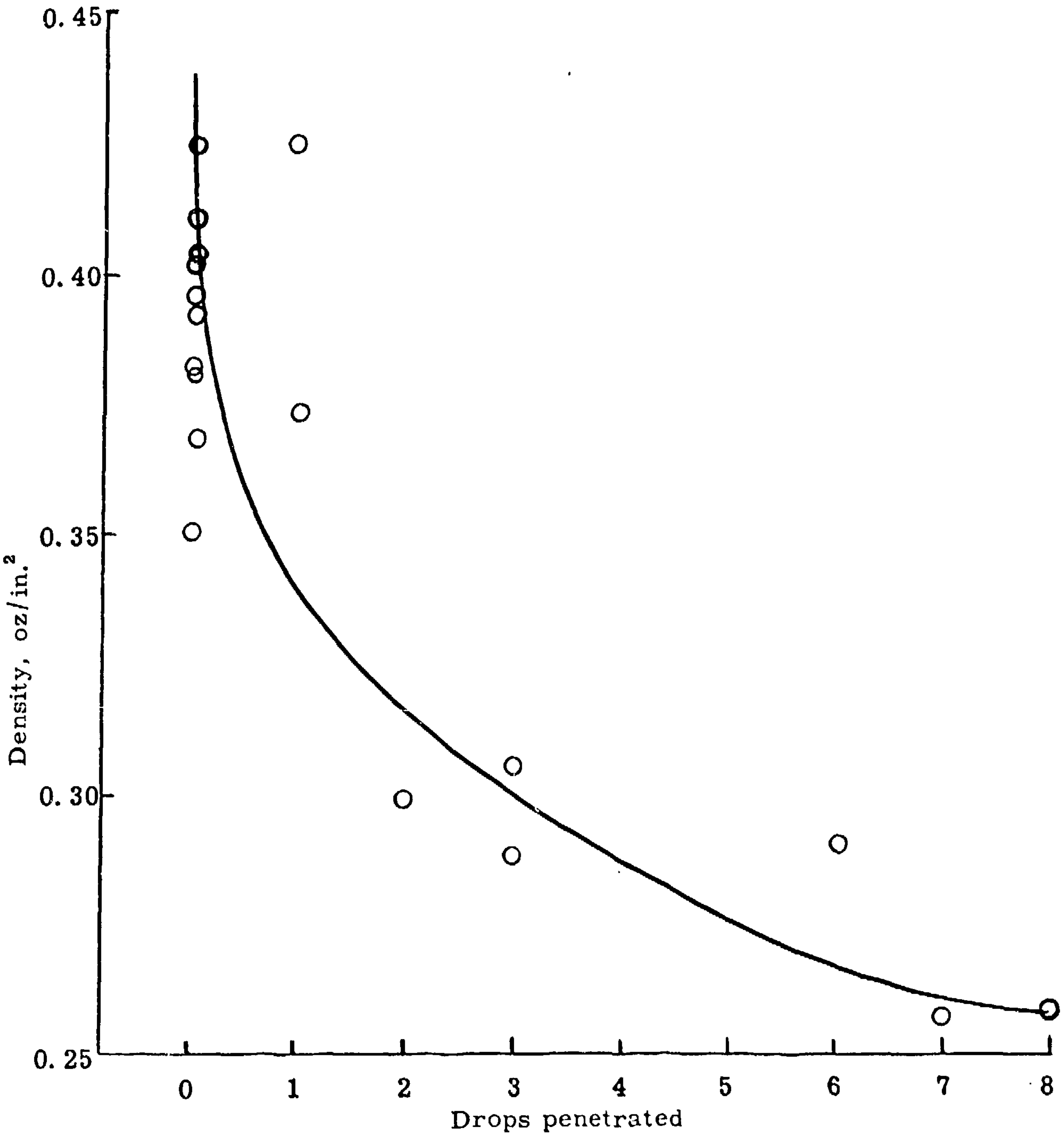

Figure III-2. Relationship Between Density and Penetration (Expulsion) by VX Agent of Fabrics Treated with 4% FC-208 Solids

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have been expected; a linear relationship might have been obtained if the measurement had been that of the time required for a drop to penetrate, instead of the number of drops penetrating in a given period (1 minute).

Penetration generally increased with increasing air permeability, a Figure III-3 indicates. Of the fifteen treated fabrics in Table III-3 that wer not penetrated (0/8) by liquid VX in the expulsion test, twelve had air permeabilities of 1 $ft^3/min/ft^2$, or less; two others had air permeabilities of 2 and 11 $ft^3/min/ft^2$. The six fabrics penetrated by one drop out of eight (1/8) had air permeabilities of 12 $ft^3/min/ft^2$, or less.

Penetration tests were made with double layers of several treated fabrics; complete resistance was indicated by the results of expulsion tests on the double layers. Thus, any of these treated fabrics would be expected to provide adequate protection in a garment if double layers were used at press points.

Comparison of Zepel B with FC-208 as a repellent indicated that, for the six cotton fabrics tested with both preparations, the Zepel B was somewhat more effective in the expulsion test with VX. Fabrics treated with Zepel B were also more resistant to deleterious weathering effects than those treated with FC-208. The breaking strength of cotton poplin treated with Zepel B was not significantly decreased when the fabric was exposed in a Weather-Ometer for 24 hours, as compared to decreases of 7% for the control fabric and 38% for the fabric treated with FC-208. Determinations of tearing strength showed a decrease of 8% for the control fabric, 8% for the fabric treated with Zepel B, and 28% for the fabric treated with FC-208.

2. Effect of mercerization

Mercerization of the cotton fabrics prior to treatment with FC-208 tended to improve their resistance to penetration by VX. Table III-4 contains data on the mercerization studies. The data show that, for the four cotton fabrics tested, resistance to penetration by VX in the expulsion test was significantly better for fabrics mercerized prior to FC-208 treatment than it was for fabrics not mercerized but treated with FC-208. Air permeability data (including measurements for several fabrics in addition to those listed in Table III-4) indicated that prior mercerization

[redacted]

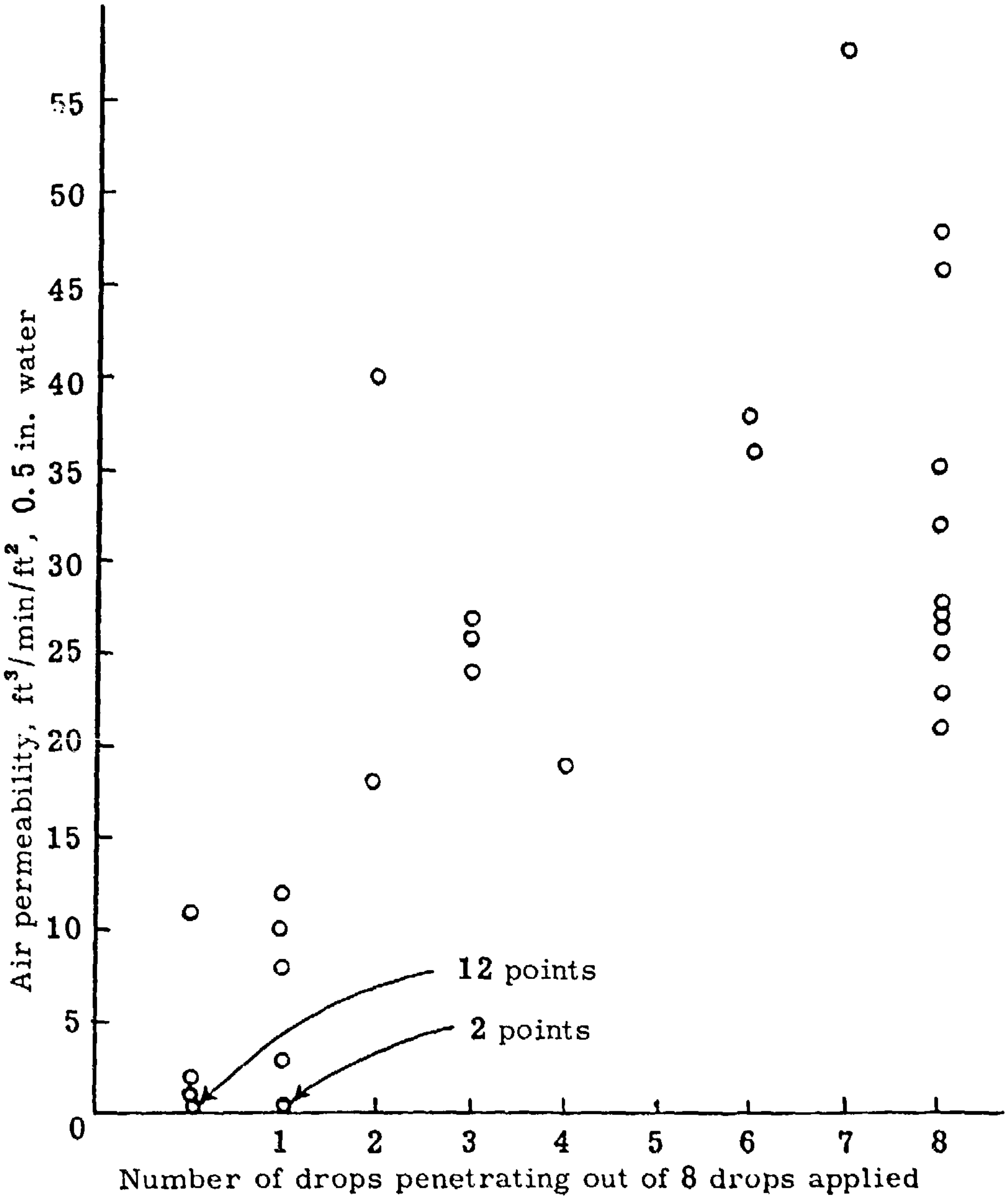

Figure III-3. Relationship Between VX Expulsion-Test Results and Air Permeability for the Treated Fabrics Listed in Table III-3.

Table III-4. Effect of Mercerization on Air Permeability and VX Penetration

Fabric	Weight, oz/yd^2	Treatment	Air permeability, ft /min/ft , 0.5 in. water	VX penetration, expulsion test[a]
Cotton poplin	5.5	untreated	6	-
	5.8	4% FC-208, padded	3	1/8
	7.2	mercerized;[b] 4% FC-208	5	0/8
Cotton sateen	8.0	untreated	18	-
	8.6	4% FC-208	18	2/8
	11.2	mercerized;[b] 4% FC-208	6	0/8
Cotton Osnaburg	7.6	untreated	39	8/8
	8.1	4% FC-208	40	2/8
	9.8	mercerized;[b] 4% FC-208	23	0/8
	10.3	mercerized;[c] 4% FC-208	25	0/8
	10.2	mercerized;[d] 4% FC-208	22	0/8
Cotton sheeting	4.0	untreated	135	8/8
	4.2	4% FC-208	58	7/8
	6.5	mercerized;[b] 4% FC-208	57	0/8
	6.6	mercerized;[c] 4% FC-208	57	1/8
	6.4	mercerized;[d] 4% FC-208	54	0/8
	5.7	mercerized,[e] shrinkage 2.6%; 4% FC-208	-	7/8
	6.1	mercerized,[e] shrinkage 5.0%; 4% FC-208	-	2/8
	6.0	mercerized,[e] shrinkage 7.3%; 4% FC-208	-	3/8
	6.4	mercerized,[b] shrinkage 11.0%; 4% FC-208	-	2/8[f]

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[a] 3 to 4 mg drops.

[b] 10 minutes in 17% sodium hydroxide solution, slack dried.

[c] 20 minutes in 17% sodium hydroxide solution, slack dried.

[d] 30 minutes in 17% sodium hydroxide solution, slack dried.

[e] 10 minutes in 17% sodium hydroxide solution, slack dried on tenter frame to control amount of shrinkage.

[f] Pin point penetration.

generally reduced the air permeability of FC-208-treated fabrics by about 50%. The weights of treated fabrics were, of course, increased by mercerization. These observations suggest that the improved resistance to penetration by liquid VX was probably caused by shrinkage and tightening of the fabric structure. To determine the minimum amount of shrinkage necessary, the 4-oz/yd^2 cotton sheeting was mercerized and dried under controlled tension so that shrinkages ranging from 2.6 to 11% were obtained. For this fabric, the shrinkage was the same in the warp and fill directions. The slack-dried fabric shrinking 11% was the most resistant to VX penetration; however, significant improvement was obtained when only 5% shrinkage was permitted. In another experiment, the VX penetration of a 3.5-oz/yd^2 cotton lawn, mercerized prior to treatment with FC-208, was only 1/8, compared to 8/8 for the unmercerized, treated, fabric.

3. Adhesives and tapes for repair kits

The need for a simple field method of repairing torn overgarments prompted a brief investigation of (1) patch materials and adhesives and (2) commercial pressure-sensitive tapes.

Two selected adhesives, EC-1729 and Splic-It, were tried in patching experiments on two treated fabrics: cotton-nylon oxford cloth treated with Quarpel, and nylon-wood pulp paper treated with Rhoplex HA-12 and FC-208. The fabrics were patched with swatches of the same material coated with either EC-1729 or Splic-It. The bonding of the patches was satisfactory, but the time required for drying and curing, 3 to 5 minutes, was considered to be too long.

Pressure-sensitive tapes offered a more convenient and rapid means for patching, and eight commercial pressure-sensitive tapes were investigated. They were evaluated qualitatively by pressing the tapes over tears in the treated cotton-nylon oxford cloth or the nylon-wood pulp paper and pulling across the patched area in the plane of the material until the patch failed. The four tapes having the best adhesion were tested quantitatively by the following procedure: Small rectangular (0.75 x 3 in.) samples of fabrics were joined by pressing a strip of pressure-sensitive tape (0.75 x 2 in.) over adjacent edges, leaving a 0.5 in. strip of fabric exposed at each end for clamping in a IP-4 Scott tester. Table III-5 shows the force necessary to pull the taped fabrics apart. Filament tape No. 880 had the best adhesion of those tested. None of these four tapes was penetrated by VX in the expulsion test.

Table III-5. Adhesion of Pressure-Sensitive Tapes to Overgarment Materials

	Strength of seal, lb, when applied to indicated fabric		
Tape	Cotton-nylon oxford cloth treated with Quarpel	Nylon-wood pulp paper, treated with Rhoplex HA-12 and FC-208	Cotton broadcloth, treated with FC-208
Mystik, plastic-coated cloth	6.4	7.2	8.4
3M No. 33, vinyl	7.5	5.3	6.4
3M No. 40, vinyl	7.2	6.5	6.6
3M No. 880, fiber-reinforced plastic	10.2	9.4	11.2

B. Inner-Layer Materials

1. Fortisan fabric

Preliminary results indicated that a 1.8-oz/yd^2 Fortisan fabric was a promising material for the inner layer. To provide sufficient material for field evaluation of finished two-layer overgarments, 500 yd of this fabric was treated with an S-330/Hycar 2671 mixture at the J. P. Stevens Company plant in Garfield, New Jersey. After some preliminary adjustment of treating conditions, a two-step spraying procedure was finally developed in which the S-330 was sprayed on one side of the fabric, the fabric was dried, Hycar 2671 latex was sprayed on the other side, and the fabric was again dried. However, samples of this treated fabric examined by the U. S. Army Natick Laboratories were not considered satisfactory with respect to resistance to penetration by agent vapor.

Generally, in laboratory work, application to the Fortisan fabric of the minimum amount of the S-330/Hycar mixture necessary to provide protection against gaseous agents (0.7 oz/yd^2) resulted in an excessive reduction in air permeability. Therefore, some studies were made to determine the effects of various amounts of S-330/Hycar 4501 mixture on the air permeability of the fabric and on the water-vapor transmission rate. Two methods of application were used: (1) all of the mixture was sprayed on one side of the fabric, and (2) half was sprayed on one side and half on the other. Table III-6 shows that the air permeability and the water-vapor transmission rate depended on both the amount of solids applied and the method of application. Application to one side reduced the air permeability and the water-vapor transmission rate more than did application to both sides. Calculations showed that an overgarment (7 yd^2 of fabric) should transmit 374 g/m^2/24 hr of water vapor for a man at rest, and 936 g/m^2/24 hr for a man doing 90,000 ft lb of work per hour. None of the treated fabrics had water-vapor transmission rates high enough to meet this requirement for adequate personal comfort.

Table III-6. Effect of S-330/Hycar 4501 Treatment of Air Permeability and Water-Vapor Transmission of Fortisan Fabric (1.8 oz/yd^2)

S-330/Hycar 4501, oz/yd^2	Weight of treated fabric, oz/yd^2	Air permeability, ft^3/min/ft^2, 0.5 in. water	Water-vapor transmission rate, g/m^2/24 hr
A. Application to one side			
0.3	2.2	19	73
0.6	2.5	7	53
0.8	2.7	< 1	31
1.1	3.0	< 1	24
B. Application to both sides			
0.4	2.3	37	100
0.7	2.6	26	83
1.1	3.0	3	65
1.4	3.3	< 1	36
C. Untreated fabric			
0	1.8	50	1399

2. Rayon nonwoven fabrics

Although rayon nonwoven fabrics did not have particularly good strength properties, they retained high air permeability even after treatment with S-330/Hycar mixtures. Table III-7 summarizes data on the physical properties and HD-vapor retention of two nonwoven fabrics. The two fabrics were made from 1.5-denier rayon fibers (Narcon) and they contained 5% Rhoplex B-15. One sample weighed 1.4 oz/yd^2 and the other weighed 2.0 oz/yd^2. The fabrics were padded to apply (1) 0.7 oz/yd^2 of an S-330/Hycar 2671 mixture, and (2) 0.61 oz/yd^2 of Hycar 2671 followed by overpadding to apply 0.09 oz/yd^2 of S-330. Both single and double layers of these treated fabrics were evaluated. No significant difference in physical properties was observed for the two different treatment procedures. However, the fabrics treated with S-330 and Hycar 2671 separately were more resistant to penetration by HD vapor than the fabrics treated with the single-bath mixture. The strength properties of all of these S-330/Hycar-treated fabrics were poorer than those of a rayon nonwoven fabric treated only with 35% Rhoplex HA-12 — a material that has been found to be a good binder.

The results of several other treatments applied to the 2.0-oz/yd^2 rayon nonwoven fabric are summarized in Table III-8. Samples of the fabric were treated with mixtures of S-330 with various binders; and the weights, thicknesses, air permeabilities, and HD-vapor retentions were measured. Of the binders studied, Hycar 4501 appeared to be the best for use with S-330 for protection against HD vapor. However, the HD-vapor retention was less than was desired. A sample treated by brushing to apply 1.2 oz/yd^2 of a mixture of activated carbon and Hycar 2671 had excellent resistance to HD vapor. It was penetrated by only 0.2 μg/cm^2 during the first 2 hours of exposure (99.2% retention) and by 1.7 μg/cm^2 (96.8% retention) during the next 4 hours. These values are comparable to those obtained with an 8.5-oz/yd^2 cotton sateen treated with XXCC-3, which is used as a standard in the determination of HD-vapor penetration in the Dawson apparatus.

[redacted]

Table III-7. Physical Properties and HD-Vapor Retention of Rayon Nonwoven Fabrics Treated with S-330/Hycar 2671

S-330/Hycar 2671 treatment	Weight of treated fabric, oz/yd²	Breaking strength, lb/in.		Elongation at break, %		Elmendorf tear, g		Air permeability, ft³/min/ft², 0.5 in. water	Abrasion resistance, cycles to rupture	Bursting strength, psi	HD-vapor[a] retention, %	
		Machine	Cross	Machine	Cross	Machine	Cross				0-2 hr	2-6 hr
Single bath[b]	1.6[d]	6.9	5.1	3.3	3.5	1824	1536	231	17	49	71.5	43.9
Single bath	2.2[e]	6.4	7.2	4.7	5.1	1568	2272	225	22	76	42.6	16.2
Single bath	3.5[f]	10.9	10.3	4.2	-	2816	2668	165	43	>120	27.2	49.8
Single bath	4.8[g]	10.6	13.4	3.3	4.7	>3200	>3200	110	95	>120	72.1	42.3
Separate baths[c]	1.7[d]	6.0	4.5	7.1	14.5	1236	2112	305	15	47	59.0	56.1
Separate baths	2.5[e]	7.2	7.2	3.5	13.5	2080	2432	230	26	66	76.0	80.6
Separate baths	3.3[f]	10.7	7.6	5.1	15.9	3200	3200	177	50	>120	81.1	63.3
Separate baths	5.2[g]	13.6	13.4	7.2	14.0	>3200	>3200	115	95	>120	78.2	67.4

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[a] Concentration of HD was 26.0 μg/l for 0-2 and 26.2 μg/l for 2-6 hr test.

[b] Fabrics treated to apply 0.7 oz/yd² of S-330/Hycar 2671 mixture. Weight ratio of Hycar 2671 to S-330 = 6.6:1.

[c] Fabrics treated to apply 0.6 oz/yd² of Hycar 2671 and overtreated to apply 0.09 oz/yd² of S-330.

[d] Single layer of rayon nonwoven weighing 1.4 oz/yd² untreated.

[e] Single layer of rayon nonwoven weighing 2.0 oz/yd² untreated.

[f] Double layer of rayon nonwoven weighing 1.4 oz/yd² untreated.

[g] Double layer of rayon nonwoven weighing 2.0 oz/yd² untreated.

Table III-8. Physical Properties and HD-Vapor Retention of 2.0 oz/yd^2 Nonwoven Rayon Fabric Containing Various Treatments

Treatment	Weight of treated fabric, oz/yd^2	Thickness, mils	Air permeability, ft^3/min/ft^2, 0.5 in. water	HD-vapor retention, %	
				0-2 hr	2-6 hr
S-330/Rhoplex B-15	2.3	17	235	48.8	56.6
S-330/Rhoplex E-32	2.4	17	206	51.2	63.0
S-330/Rhoplex HA-12	2.4	22	229	44.5	55.8
S-330/Hycar 4501	3.0	17	233	69.5	72.8
Carbon/Hycar 2671	3.4	23	85	99.2	96.8

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[a] 0.7 oz/yd^2 of 1:6.6 S-330/binder mixture.

[b] 1.2 oz/yd^2 of 5:1 carbon/Hycar 2671 mixture.

[c] Concentration of HD was 21.2 µg/l for 0.2 hr test and 22.1 µg/l for 2-6 hour test.

3. Polyurethane foams

Thin layers of polyurethane foam were considered to have potential utility as inner-layer material. It was envisioned that a suitable foam would have a small cell size, a high proportion of closed cells, and would be flexible. Such a foam should offer resistance to penetration by CW agents by presenting a devious and restricted passage, but should still have adequate air permeability. Resistance to agents should be assisted by impregnation with absorbents.

Several foam formulations were investigated to determine what combination of ingredients would give a product with the desired properties. The basic foam formulation adopted consisted of the following materials:

Nicex PPG 2025 polyether	30.0 parts
Hylene TM-toluene diisocyanate	11.0 parts
Water	0.74 parts
Triethylenediamine	0.17 parts
D-22 tin dilaurate	Variable
L-520 silicone oil	Variable

All ingredients except water were premixed. Water was then added, the mixture was stirred, poured into a paper container, and allowed to foam. The foams were cured at room temperature for 2 to 3 hours and then at 80°C for 30 minutes. A practical concentration of amine catalyst, which determines the rate of carbon dioxide generation, was established by preliminary trials. Then a series of foams was prepared with a range of tin catalyst and silicone oil concentrations. The tin affected the gelation rate of the polymer, and the silicone influenced the size of the cells and the stability of the foam.

[redacted]

The optimum concentration of the D-22 tin catalyst was found to be 0.5% by weight, and that of the L-520 silicone oil was 0.4 to 0.6%. At these concentrations, foams of uniform cell structure having approximately equal amounts of open and closed cells were prepared. Microscopic examination revealed that the flow of polymer into the ribs of the cells was adequate for structural strength.

Evaluation of polyurethane foams for resistance to penetration by agents was done only in two-layer composites with outer layers of woven fabrics. Data on these systems are included in Section IV-C.

4. Scrim reinforcing for nonwoven fabrics and polyurethane foams

Methods of applying nylon scrim to nonwoven fabrics and polyurethane foams in order to improve their durability were considered. Several types of adhesives were evaluated for bonding a 4.3-oz/yd^2 nylon scrim to a rayon nonwoven fabric. Rhoplex E-32* was found to be an effective adhesive for bonding scrim to a nonwoven web as determined by laboratory studies. Nylon scrim can be flame bonded to polyurethane foam by presently existing commercial methods, and no attempt was made to bond nylon scrim to foam with an adhesive.

C. Evaluation of Two-Layer Systems

Preliminary studies, described earlier in this report, indicated that a two-layer system for a durable overgarment to provide protection against toxic liquids and vapors was superior to a single-layer garment. Toward the close of this project, work was concentrated on the evaluation of two-layer systems composed of the materials that had been found to be most promising in the preliminary studies. For the outer layer, a slack-mercerized, 6.5-oz/yd^2 cotton sheeting treated with Zepel B was selected for intensive evaluation with several candidate inner-layer materials. For the inner layer, the following materials were selected:

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* Prepared by adding 5.4 parts of Methocel slurry (8 parts of ethanol to 1 part of Methocel 4000) to 100 parts of Rhoplex E-32 and then adding 1.0 part of oxalic acid.

[redacted]

(1) a 2.0-oz/yd^2 rayon nonwoven web made from $1\frac{9}{16}$-in., 3.0 denier fibers, (2) a 1.8-oz/yd^2 Fortisan fabric, and (3) a 4.6-oz/yd^2 polyurethane foam/nylon fabric laminate. Activated carbon, S-330, and CC-2 were used to treat the inner layer, with and without Hycar 4501 as binder. Some additional work was done with certain other outer-layer fabrics and inner-layer binders.

1. Two-layer systems with Zepel B-treated cotton fabric as the outer layer and various materials as the inner layer

a. Preparation of treating baths

(1) Activated carbon bath

Twelve parts of Protovac PV-432 (casein) was soaked in 86.8 parts of water for 5 to 10 minutes. Then 1.2 parts of ammonium hydroxide (28%) was added to the solution and the mixture was heated to 180°F with stirring. The solution was held at 180°F for 20 minutes and then cooled to room temperature.

The casein solution was added to a slurry of 250 parts of carbon, which had been ball milled in 550 parts of water. The mixture was stirred until uniform, and finally 100 g of water was added. The final solution contained 25% carbon and 1.2% casein.

(2) Carbon/Hycar 4501 bath

The carbon/Hycar 4501 bath was prepared as described above except 100 g of Hycar 4501 (50% solids) was substituted for the final 100 g of water. The final bath contained 25% carbon, 1.2% casein, and 5% Hycar 4501.

(3) S-330 bath

To a mixture containing 25 parts of S-330 and 64 parts of water which had been ball milled for 24 hours, 10 parts of an Elvanol 50-42 solution (10% Elvanol) and 1 part of Santomerse SX were added with stirring. The final bath contained 25% S-330, 1% Elvanol, and 1% Santomerse SX.

(4) CC-2 solution

A solution containing 27% CC-2 (53.2% total solids) was prepared as described in Laboratory Directive No. 112[1] and diluted with water as required.

(5) Hycar 4501

Hycar 4501 (50% solids) was diluted to the desired solids by the addition of water.

b. Application procedures

Samples of the nonwoven fabric and the polyurethane foam/nylon fabric laminate were treated by dipping them in the solutions and then putting them through a Butterworth Padder to obtain the desired add-ons. The treatments were applied to the samples of the Fortisan fabric with a brush.

(1) Carbon, Carbon/Hycar 4501, CC-2, and S-330 mixture

The concentration of the baths used for treating the samples with carbon, carbon/Hycar 4501 mixture, S-330, and CC-2 are given in Table III-9 along with the solids applied to each material.

(2) Hycar 4501 and S-330 or CC-2

Samples of the rayon nonwoven, polyurethane foam, and Fortisan fabric were treated to apply 0.6 oz/yd^2 of Hycar 4501 and then overtreated with S-330 or CC-2. A bath containing 10% solids was used for treating

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[1] Laboratory Directive No. 112, "Laboratory Impregnation of Fabrics with CC-2 by the Aqueous Suspension Process," U. S. Army Chemical Corps Technical Command, Protective Division.

[redacted]

[redacted]

Table III-9. Concentration of Treating Baths and Solids Add-on for Carbon, S-330, CC-2, and Carbon/Hycar Treatments

Material	Solids in treating bath, %	Attempted add-on, oz/yd^2
A. Carbon[a]		
Rayon nonwoven	6.25	1.0
	6.25	0.5
Polyurethane foam	15.0	1.0
	15.0	0.5
Fortisan	25.0	1.0
	25.0	0.5
B. Carbon/Hycar 4501[b]		
Rayon nonwoven	5.0	0.5
	10.0	1.0
Polyurethane foam	15.0	0.5
	15.0	1.0
Fortisan	10.0	0.5
	10.0	1.0
C. S-330[c]		
Rayon nonwoven	12.5	1.0
	6.25	0.5
Polyurethane foam	15.0	1.0
	15.0	0.5
Fortisan	25.0	1.0
	25.0	0.5
D. CC-2[d]		
Rayon nonwoven	13.5	1.0
	6.2	0.5
Polyurethane foam	28.0	1.0
	28.0	0.5
Fortisan	22.4	1.0
	12.2	0.5

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[a] Treated samples dried at room temperature.

[b] Treated samples dried 5 minutes at 121°C.

[c] Treated samples dried 2 minutes at 121°C.

[d] Treated samples dried 6 minutes at 90°C. Solids in bath are CC-2 solids only.

[redacted]

the rayon nonwoven samples and a bath containing 20% solids was used for treating the polyurethane foam and the Fortisan samples. The samples were dried for 2 minutes at 250°F after application of the Hycar 4501. The concentration of baths used for overpadding the Hycar 4501-treated samples with S-330 and CC-2 are given in Table III-10 along with the solids applied.

c. Results and discussion

The weight, air permeability, resistance to VX liquid, and resistance to HD vapor of each of the 36 two-layer systems with an outer layer of a 6.5-oz/yd^2, mercerized cotton fabric treated with 4% Zepel B and the different inner layer materials described above are given in Tables III-11 through III-16 and are summarized below.

The total weights of the two-layer systems ranged from 8.6 to 13.3 oz/yd^2. Systems with the polyurethane foam/nylon fabric laminate as the inner layers were the heaviest, ranging in weight from 11.7 to 13.3 oz/yd^2. Systems with the nonwoven and Fortisan fabrics as the inner layers had about the same weights, 8.6 to 10.5 oz/yd^2.

The air permeabilities of the two-layer systems with the Fortisan fabric, the nonwoven fabric, and the foam/fabric laminate as the inner layers ranged, respectively, from 0.5 to 3, 13 to 17, and 14 to 17.5 ft^3/min/ft^2.

All of the combinations are considered to have satisfactory resistance to VX liquid. The combination containing the Fortisan fabric treated to apply 1.0 oz/yd^2 of carbon was penetrated by 1 out of 8 drops of VX in the expulsion test, and the combination containing the Fortisan fabric treated to apply 1.0 oz/yd^2 of S-330 was penetrated by 1 out of 6 drops of VX in the drop test and 1 out of 8 drops in the expulsion tests. However, the penetrations were probably due to nonuniform treatments, since the combinations containing the Fortisan fabric treated to apply 0.5 oz/yd^2 of carbon or S-330 were not penetrated by the agent. None of the other combinations was penetrated by VX in the drop or expulsion tests.

[redacted]

Table III-10. Concentrations of Baths Used for Overtreating Hycar 4501-Treated Samples

	Material	Solids in treating bath, %	Add-on, oz/yd^2
A.	S-330[a]		
	Rayon nonwoven	5.0	0.2
		10.0	0.5
	Polyurethane foam	10.0	0.2
		10.0	0.5
	Fortisan	25.0	0.2
		25.0	0.5
B.	CC-2[b]		
	Rayon nonwoven	10.0	0.2
		15.0	0.5
	Polyurethane foam	10.0	0.2
		25.0	0.5
	Fortisan	20.0	0.2
		20.0	0.5

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[a] Treated samples dried 2 minutes at 121°C.

[b] Treated samples dried 6 minutes at 90°C. Solids in bath are CC-2 solids only.

[redacted]

Table III-11. Properties and CW Resistance of Two-Layer Systems with Zepel B-Treated Cotton Fabric as the Outer Layers and Different Carbon-Treated Materials as the Inner Layers

	Inner layer				Resistance to VX liquid[c]			Resistance to HD vapor					
								Test conditions[d]					
					Drop test		Expulsion test	HD vapor conc., µg/l		HD vapor penetration, µg/cm²		HD vapor retention,[e] %	
Material[a]	Carbon add-on, oz/yd²	Treated weight, oz/yd²	Total weight,[b] oz/yd²	Air permeability, ft³/min/ft², 0.5 in. water	Specimens penetrated	Drops penetrated	Specimens penetrated	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
A	0.1	2.1	8.6	13.0	0/2	0/6	0/8	23.5	21.4	0.8	7.9	97.2	84.6
	0.3	2.3	8.8	15.0	0/2	0/6	0/8	23.5	21.4	0.2	0.2	99.3	99.6
B	0.4	2.2	8.7	2.5	0/2	0/6	0/8	23.5	21.4	0.1	0.3	99.6	99.4
	0.7	2.5	9.0	2.0	0/2	0/6	1/8	23.5	21.4	0.5	2.8	98.2	94.6
C	0.8	5.4	11.9	14.9	0/2	0/6	0/8	22.2	22.0	0.7	9.0	97.0	83.0
	1.0	5.6	12.1	14.0	0/2	0/6	0/8	22.2	22.0	0.1	<0.1	>99.6	>99.8

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[a] A - Rayon nonwoven fabric; B - Fortisan fabric; C - Polyurethane foam/nylon fabric.

[b] Outer layer weighed 6.5 oz/yd².

[c] Specimens or drops penetrated/specimens or drops tested. 3 to 4 mg drops.

[d] Flow rate of 0.6 l/hr/cm².

[e] $\%\ \text{retention} = 100 - \left[\dfrac{\text{penetration in } \mu g/cm^2}{\mu g/l \times 0.6/l/hr/cm^2 \times hr} \times 100\right]$.

Table III-12. Properties and CW Resistance of Two-Layer Systems with Zepel B-Treated Cotton Fabric as the Outer Layers and Different S-330-Treated Materials as the Inner Layers

					Resistance to VX liquid[c]			Resistance to HD vapor					
								Test conditions[d]					
	Inner layer				Drop test		Expulsion test	HD vapor conc., μg/l		HD vapor penetration μg/cm^2		HD vapor retention,[e] %	
Material[a]	S-330 add-on, oz/yd^2	Treated weight, oz/yd^2	Total weight,[b] oz/yd^2	Air permeability ft^3/min/ft^2, 0.5 in. water	Specimens penetrated	Drops penetrated	Specimens penetrated	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
A	0.3	2.3	8.8	15.0	0/2	0/6	0/8	23.5	21.4	11.1	11.8	60.6	77.0
	0.5	2.5	9.0	14.0	0/2	0/6	0/8	23.0	22.2	10.4	15.4	62.3	71.1
B	0.3	2.1	8.6	3.0	0/2	0/6	0/8	23.0	22.2	10.2	12.8	63.0	76.0
	0.6	2.4	8.9	1.0	0/2	1/6	1/8	23.0	22.2	5.8	7.4	79.0	86.1
C	0.6	5.2	11.7	17.0	0/2	0/6	0/8	22.2	22.0	1.2	0.2	95.5	99.6
	1.3	5.9	12.4	17.0	0/2	0/6	0/8	22.2	22.0	<0.1	<0.1	99.6	99.8

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[a] A - Rayon nonwoven fabric; B - Fortisan fabric; C - polyurethane foam/nylon fabric.

[b] Outer layer weighed 6.5 oz/yd^2.

[c] Specimens or drops penetrated/specimens tested or drops applied, 3 to 4 mg drops.

[d] Flow rate 0.6 l/hr/cm^2.

[e] $\% \text{ retention} = 100 - \left[\dfrac{\text{penetration in } \mu g/cm^2}{\mu g/l \times 0.6 \; l/hr/cm^2 \times hr} \times 100 \right]$.

Table III-13. Properties and CW Resistance of Two-Layer Systems with Zepel B-Treated Cotton Fabric as the Outer Layers and Different CC-2-Treated Materials as the Inner Layers

Material[a]	Inner layer		Total weight,[c] oz/yd²	Air permeability, ft³/min/ft², 0.5 in. water	Resistance to VX liquid[d]			Resistance to HD vapor					
					Drop test		Expulsion test	Test conditions[e]					
								HD vapor conc., μg/l		HD vapor penetration, μg/cm²		HD vapor retention,[f] %	
	CC-2 add-on,[b] oz/yd²	Treated weight, oz/yd²			Specimens penetrated	Drops penetrated	Specimens penetrated	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
A	0.4	2.7	9.2	13.0	0/2	0/6	0/8	23.0	22.2	4.7	4.2	83.0	92.1
	1.0	3.9	10.4	14.5	0/2	0/6	0/8	22.7	22.1	1.4	2.1	95.0	96.0
B	0.3	2.4	8.9	2.0	0/2	0/6	0/8	22.7	22.1	3.3	4.2	87.9	91.9
	1.1	4.0	10.5	>1.0	0/2	0/6	0/8	23.0	22.2	4.6	8.1	83.3	84.8
C	0.7	5.9	12.4	16.5	0/2	0/6	0/8	22.2	22.0	0.8	1.5	97.0	97.2
	1.1	6.8	13.3	16.5	0/2	0/6	0/8	22.2	22.0	0.3	0.7	98.9	98.7

---

[a] A - Rayon nonwoven fabric; B - Fortizan fabric; C - Polyurethane foam/nylon laminate.

[b] CC-2 applied as XXCC-3. 1.0 oz/yd² of CC-2 equals 1.97 oz/yd² of XXCC-3.

[c] Outer layer weighed 6.5 oz/yd²

[d] Specimens or drops penetrated/specimens tested or drops applied, 3 to 4 mg drops.

[e] Flow rate 0.6 l/hr/cm².

[f] $$\% \text{ retention} = 100 - \left[\frac{\text{penetration in } \mu g/cm^2}{\mu g/l \times 0.6\ l/hr/cm^2 \times hr} \times 100\right].$$

Table III-14. Properties and CW Resistance of Two-Layer Systems with Zepel-B-Treated Cotton Fabric as the Outer Layers and Different Carbon/Hycar 4501 Treated Materials as the Inner Layers

Material[a]	Inner layer		Total weight,[c] oz/yd²	Air permeability, ft³/min/ft², 0.5-in. water	Resistance to VX liquid[d]			Resistance to HD vapor, test conditions[e]					
	Carbon/ Hycar 4501 add-on,[b] oz/yd²	Treated weight, oz/yd²			Drop test		Expulsion test	HD vapor conc., µg/l		HD vapor penetration µg/cm²		HD vapor retention,[f] %	
					Specimens penetrated	Drops penetrated	Specimens penetrated	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
A	0.5	2.5	9.0	17.0	0/2	0/6	0/8	24.1	22.9	0.1	3.8	99.7	93.3
	0.6	2.6	9.1	15.5	0/2	0/6	0/8	24.1	22.9	<0.1	<0.1	>99.7	>99.8
B	0.8	2.6	9.1	1.0	0/2	0/6	0/8	24.1	23.6	0.3	1.8	99.0	96.9
	0.9	2.7	9.2	0.5	0/2	0/6	0/8	24.1	22.9	<0.1	0.6	>99.7	98.4
C	0.6	5.2	11.7	16.5	0/2	0/6	0/8	22.2	22.0	1.6	14.8	94.0	83.3
	1.2	5.8	12.3	15.0	0/2	0/6	0/8	22.2	22.0	0.2	3.1	99.2	94.1

---

[a] A - Rayon nonwoven fabric; B - Fortisan fabric; C - Polyurethane foam/nylon laminate.

[b] 5:1 solids ratio of carbon to Hycar 4501.

[c] Outer layer weighed 6.5 oz/yd².

[d] Specimens or drops penetrated/specimens tested or drops applied, 3 to 4 mg drops.

[e] Flow rate 0.6 l/hr/cm².

[f] $\% \text{ retention} = 100 - \left[\frac{\text{penetration in } \mu g/cm^2}{\mu g/l \times 0.6\ l/hr/cm^2 \times hr} \times 100 \right]$.

Table III-15. Properties and CW Resistance of Two-Layer Systems with Zepel-B-Treated Cotton Fabric as the Outer Layers and Different S-330/Hycar 4501 Treated Materials as the Inner Layers

	Inner layer				Resistance to VX liquid[d]			Resistance to HD vapor					
								Test conditions[e]					
					Drop test		Expulsion test	HD vapor conc., µg/l		HD vapor penetration µg/cm²		HD vapor retention,[f] %	
Material[a]	S-330/ Hycar 4501 add-on,[b] oz/yd²	Treated weight, oz/yd²	Total weight,[c] oz/yd²	Air permeability, ft³/min/ft², 0.5 in. water	Specimens penetrated	Drops penetrated	Specimens penetrated	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
A	0.9	2.9	9.4	14.0	0/2	0/6	0/8	24.1	22.9	0.1	<0.1	>99.7	>99.8
	1.2	3.2	9.7	14.0	0/2	0/6	0/8	24.1	23.6	<0.1	<0.1	>99.7	>99.8
B	0.7	2.5	9.0	>1.0	0/2	0/6	0/8	24.1	22.9	0.3	0.8	98.9	98.6
	0.9	2.7	9.2	>1.0	0/2	0/6	0/8	24.1	22.9	1.7	4.5	94.1	92.2
C	1.3	5.9	12.4	17.5	0/2	0/6	0/8	22.2	22.0	0.4	0.1	98.5	99.8
	1.6	6.2	12.7	17.0	0/2	0/6	0/8	22.2	22.0	0.4	0.1	98.5	99.8

---

[a] A - Rayon nonwoven fabric; B - Fortisan fabric; C - Polyurethane foam/nylon fabric laminate.

[b] Hycar 4501 was applied to give an approximate add-on of 0.6 oz/yd² and then the S-330 was applied to give an approximate add-on of 0.2 or 0.5 oz/yd².

[c] Outer layer weighed 6.3 oz/yd².

[d] Specimens or drops penetrated/specimens tested or drops applied, 3 to 4 mg drops.

[e] Flow rate 0.6 l/hr/cm².

[f] $$\% \text{ retention} = 100 - \left[\frac{\text{penetration in } \mu g/cm^2}{\mu g/l \times 0.6\ l/hr/cm^2 \times hr} \times 100 \right].$$

Table III-16. Properties and CW Resistance of Two-Layer Systems with Zepel B-Treated Cotton Fabric as the Outer Layer and Different CC-2/Hycar 4501 Treated Materials as the Inner Layers

	Inner layer				Resistance to VX liquid[d]			Resistance to HD vapor					
								Test conditions[e]					
					Drop test		Expulsion test	HD vapor conc., μg/l		HD vapor penetration, μg/cm²		HD vapor retention,[f] %	
Material[a]	CC-2/ Hycar 4501 add-on,[b] oz/yd²	Treated weight, oz/yd²	Total weight,[c] oz/yd²	Air permeability, ft³/min/ft², 0.5 in. water	Specimens penetrated	Drops penetrated	Specimens penetrated	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
A	0.9	2.9	9.4	15.0	0/2	0/6	0/8	22.2	22.0	0.3	3.4	98.9	91.7
	1.2	3.2	9.7	15.5	0/2	0/6	0/8	22.2	22.0	0.2	0.4	99.2	99.2
B	0.7	2.5	9.0	>1.0	0/2	0/6	0/8	24.1	23.6	4.4	11.0	84.8	80.9
	0.9	2.7	9.2	>1.0	0/2	0/6	0/8	24.1	23.6	<0.1	<0.1	>99.7	>99.8
C	1.3	5.9	12.4	17.0	0/2	0/6	0/8	22.2	22.0	3.4	15.0	87.2	71.6
	1.6	6.2	12.7	17.5	0/2	0/6	0/8	22.2	22.0	1.5	6.0	94.4	88.6

---

[a] A - Rayon nonwoven fabric; B - Fortisan fabric; C - polyurethane foam/nylon fabric laminate.

[b] Hycar 4501 was applied to give an approximate add-on of 0.6 oz/yd² and then the CC-2 was applied as XXCC-3 to give add-ons of approximately 0.98 and 1.97 oz/yd². *1 oz/yd² of CC-2 equals 1.97 oz/yd² of XXCC-3.*

[c] Outer layer weighed 6.5 oz/yd².

[d] Specimens or drops penetrated/specimens tested or drops applied, 3 to 4 mg drops.

[e] Flow rate 0.6 l/hr/cm².

[f] $$\% \text{ retention} = 100 - \left[\frac{\text{penetration in } \mu g/cm^2}{\mu g/l \times 0.6 \; l/hr/cm^2 \times hr} \times 100 \right].$$

Satisfactory HD-vapor resistance (>95% retention) was obtained with some of the combinations containing the carbon-treated inner layers, but the carbon did not adhere well to the inner-layer materials, especially to the nonwoven and Fortisan fabrics. For satisfactory HD-vapor resistance the results indicate that the nonwoven and Fortisan fabrics must contain about 0.5 oz/yd^2 of carbon, and the foam/fabric laminate must contain about 1.0 oz/yd^2 of carbon. With the S-330 treatment, only the foam/fabric laminate gave satisfactory resistance to HD vapor, possibly because of loss of S-330 by the other materials before the evaluations were made. Samples with Hycar 4501 as binder for the S-330 had in general better resistance to HD vapor than samples without a binder. This was probably due to better adherence of the S-330 to the materials.

The rayon nonwoven fabric and the foam/fabric laminate containing about 1.0 oz/yd^2 of CC-2 provided satisfactory HD-vapor resistance in the two-layer systems, but the Fortisan fabric containing about 1.0 oz/yd^2 of CC-2 was not satisfactory. The use of Hycar 4501 with CC-2 improved the HD-vapor resistance of the Fortisan fabric to a satisfactory level. However, the Hycar had no apparent effect on the HD-vapor resistance of CC-2-treated nonwoven fabrics; and it significantly decreased the HD-vapor resistance of the CC-2-treated foam/fabric laminates.

With the exception of the systems having inner layers treated with carbon and S-330 without Hycar 4501 as binder, the systems found to have good resistance to HD vapor in the above studies were evaluated for resistance to the vapor from drops of HD liquid. In addition, a sample of the polyurethane foam/nylon fabric laminate treated to apply 2.0 oz/yd^2 of the carbon/Hycar 4501 mixture was evaluated in a two-layer system with Zepel B-treated cotton fabric as the outer layer. The results are given in Table III-17. The systems having inner layers treated with S-330 or carbon without Hycar 4501 binder that had good resistance to HD vapor, were not evaluated for resistance to the vapor from drops of HD liquid because of the poor adhesion of the S-330 and carbon to the inner-layer materials.

As shown by the results in Table III-17 the two-layer systems with the Fortisan and nonwoven fabrics treated with Hycar 4501 and CC-2 were penetrated, respectively, by 480 and 316 μg, respectively, of vapor from a 4-mg drop of HD liquid, compared to penetration of the Zepel B-treated cotton fabric outer layer alone by only 116 μg of vapor. The resistance of the other two-layer combinations was only slightly better or not significantly different from the resistance of the Zepel B-treated cotton fabric alone.

[redacted]

[redacted]

Table III-17. Resistance of Two-Layer Systems to Penetration by Vapor from Drops of HD Liquid

Inner layer[a]	Treatment	Vapor penetration per drop of HD liquid[b]	
		µg	%
Rayon nonwoven fabric	0.6 oz/yd^2 Hycar 4501 and 0.5 oz/yd^2 CC-2	316	7.9
	0.6 oz/yd^2 Hycar 4501 and 0.2 oz/yd^2 S-330	172	4.3
	0.6 oz/yd^2 Hycar 4501 and 0.5 oz/yd^2 S-330	80	2.0
	0.5 oz/yd^2 carbon/Hycar 4501[c]	112	2.8
	1.0 oz/yd^2 carbon/Hycar 4501[c]	136	3.4
Fortisan fabric	0.6 oz/yd^2 Hycar 4501 and 0.5 oz/yd^2 CC-2	480	12.0
	0.6 oz/yd^2 Hycar 4501 and 0.2 oz/yd^2 S-330	136	3.4
	0.5 oz/yd^2 carbon/Hycar 4501[c]	140	3.5
	1.0 oz/yd^2 carbon/Hycar 4501[c]	112	2.8
Polyurethane foam/nylon fabric	0.6 oz/yd^2 Hycar 4501 and 0.2 oz/yd^2 S-330	84	2.1
	0.6 oz/yd^2 Hycar 4501 and 0.5 oz/yd^2 S-330	48	1.2
	1.0 oz/yd^2 carbon/Hycar 4501[c]	32	0.8
	2.0 oz/yd^2 carbon/Hycar 4501[c]	140	3.5
	1.0 oz/yd^2 CC-2	108	2.7

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[a] Outer layer was Zepel B-treated woven cotton fabric.

[b] 3 to 4 mg drops used in test. Duration of test was 24 hours at 35°C. The Zepel B-treated cotton fabric outer layer (without an inner layer) was penetrated by 116 µg (2.9%) of HD vapor.

[c] 5:1 solids ratio of carbon to Hycar 4501.

[redacted]

Systems with the 7 inner layers listed below and with Zepel B-treated cotton fabric as the outer layer were evaluated for resistance to the vapors from drops of VX and GB liquids. The results are given in Table III-18.

1. Rayon nonwoven fabric treated to apply 0.6 oz/yd^2 of Hycar 4501 and overtreated to apply 0.5 oz/yd^2 of S-330.

2. Rayon nonwoven fabric treated to apply 0.6 oz/yd^2 of Hycar 4501 and overtreated to apply 0.5 oz/yd^2 of CC-2.

3 and 4. Rayon nonwoven fabric treated to apply 1.0 or 2.0 oz/yd^2 of the carbon/Hycar 4501 mixture.

5. Polyurethane foam/nylon fabric laminate treated to apply 0.6 oz/yd^2 of Hycar 4501 and overtreated to apply 0.5 oz/yd^2 of S-330.

6 and 7. Polyurethane foam/nylon fabric laminate treated to apply 1.0 or 2.0 oz/yd^2 of the carbon/Hycar 4501 mixture.

No treated Fortisan fabrics were included in these evaluations. The data given previously showed that the two-layer systems with inner layers of treated Fortisan fabrics had low air permeabilities, they did not give any better protection from HD vapor than those containing the rayon nonwoven fabric or the polyurethane foam/nylon fabric laminate, and the treatments adhered better to the other inner-layer materials.

When evaluated as a single layer, the Zepel B-treated cotton fabric used as the outer layer in these samples was penetrated by 52 μg of vapor from a 4-mg drop of VX and by 592 μg of vapor from a drop of GB. The use of the Hycar/S-330-treated nonwoven fabric with the Zepel B-treated cotton fabric provided little additional resistance to penetration. However, the Hycar/S-330-treated laminate in combination with the Zepel-treated cotton fabric was penetrated by only 6.8 μg of VX vapor, but it was penetrated by 320 μg of GB vapor from 4-mg drops. The two-layer systems containing the nonwoven fabric or the laminate treated with the carbon/Hycar 4501 mixture were penetrated by only 2.0-3.6 μg of VX vapor and 64-200 μg of GB vapor from drops of the agents. Hence, the Hycar 4501/carbon treatment gave better protection against the vapors from drops of VX and GB than the Hycar 4501/S-330 treatments. On the nonwoven fabric, it also gave better protection than the Hycar 4501/CC-2 treatment.

Table III-18. Resistance of Two-Layer Systems to Penetration by Vapor from Drops of VX and GB Liquids

Inner layer[a]	Treatment	Vapor penetration[b] per drop of agent: VX liquid[c] μg	VX liquid[c] %	GB liquid[d] μg	GB liquid[d] %
Rayon nonwoven fabric	0.5 oz/yd² CC-2 and 0.6 oz/yd² Hycar 4501	3.6	0.09	332	8.3
	0.5 oz/yd² S-330 and 0.6 oz/yd² Hycar 4501	48.0	1.2	476	11.9
	1.0 oz/yd² carbon/Hycar 4501[e]	2.8	0.07	200	5.0
	2.0 oz/yd² carbon/Hycar 4501[e]	2.0	0.05	64	1.6
Polyurethane foam/nylon fabric laminate	0.5 oz/yd² S-330 and 0.6 oz/yd² Hycar 4501	6.8	0.17	320	8.0
	1.0 oz/yd² carbon/Hycar 4501[e]	2.8	0.07	156	3.9
	2.0 oz/yd² carbon/Hycar 4501[e]	3.6	0.09	100	2.5

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[a] Outer layer was Zepel B-treated woven cotton fabric.

[b] 3 to 4 mg drops used in test.

[c] Duration of test was 24 hr at 35°C. The Zepel B-treated cotton fabric outer layer (without an inner layer) was penetrated by 52 μg of a 4-mg drop of VX (1.3%).

[d] Duration of test was 6 hr at room temperature. The Zepel B-treated cotton fabric was penetrated by 592 μg of a 4-mg drop of GB (14.8%).

[e] 5:1 solids ratio of carbon to Hycar 4501.

2. Effect of accelerated aging of two-layer systems on their resistance to penetration by HD vapor

Several two-layer systems having a Zepel B-treated cotton as the outer layer and treated rayon nonwoven fabric or polyurethane foam/nylon fabric laminates as the inner layer were stored at 80°C in sealed containers in the presence of an uncovered beaker of water. The resistances to penetration by HD vapor after storage, as determined in the Dawson apparatus, are shown in Table III-19 for some of these systems. In systems having S-330 in the inner layer, severe degradation occurred because of hydrolysis of the S-330 to hydrochloric acid; the cotton outer layer became discolored and was easily torn by hand. Because of this degradation, the HD-vapor penetration of these systems was not determined. The foam/fabric system with carbon/Hycar 4501 and the rayon nonwoven-fabric systems with Hycar 4501 and CC-2 were significantly less resistant to HD vapor after aging. The other systems were not significantly affected.

3. Effect of perspiration on vapor resistance of carbon/Hycar 4501-treated systems

a. HD vapor

Samples of a rayon nonwoven fabric treated with 1.0 oz/yd^2 and 2.0 oz/yd^2 of the carbon/Hycar 4501 mixture were evaluated for resistance to HD vapor with the Dawson apparatus before and after exposure to body perspiration. For comparison a polyurethane foam/nylon fabric laminate treated with 2.0 oz/yd^2 of the carbon/Hycar 4501 mixture was evaluated under the same conditions. Three samples of each material were prepared and three different individuals wore a sample of each material in contact with the skin for three working days. The individuals who wore these specimens do janitorial type work, which represents moderate activity. The data for the HD-vapor resistance of the exposed and unexposed materials are given in Table III-20. Exposure to body perspiration did not decrease the resistance to HD-vapor of the carbon/Hycar treated nonwoven fabric or the polyurethane foam/nylon fabric laminate.

[redacted]

[redacted]

Table III-19. HD-Vapor Resistance of Two-Layer Systems with Zepel B-Treated Cotton Fabric as Outer Layer and Various Inner Layers Before and After Accelerated Aging for 16 Hours

		Resistance to HD vapor							
		HD-vapor penetration, $\mu g/cm^2$				HD-vapor retention, %			
		Before accelerated aging		After accelerated aging		Before accelerated aging		After accelerated aging	
Inner layer material	Treatment	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
[illegible]n nonwoven fabric	1.0 oz/yd^2 carbon/Hycar 4501[b]	<0.1	<0.1	<0.1	0.6	>99.7	>99.8	>99.6	98.9
Rayon nonwoven fabric	2.0 oz/yd^2 carbon/Hycar 4501	<0.1	0.2	0.1	0.3	>99.6	99.5	>99.6	99.4
Rayon nonwoven fabric	0.6 oz/yd^2 Hycar 4501 and 0.5 oz/yd^2 CC-2	0.2	0.4	2.3	14.6	98.9	99.2	91.3	73.0
Polyurethane foam/nylon fabric laminate	1.0 oz/yd^2 carbon/Hycar 4501	0.2	3.1	6	18.9	99.2	94.1	77.4	66.2
Polyurethane foam/nylon fabric laminate	2.0 oz/yd^2 carbon/Hycar 4501	<0.1	<0.1	<0.1	0.1	>99.6	>99.8	>99.6	99.8

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[a] Sample stored in sealed container containing beaker of water (100 ml) at 80°C.

[b] 5:1 solids ratio of carbon to Hycar 4501.

Table III-20. HD-Vapor Resistance of Two-Layer Systems with Zepel B-Treated Cotton Fabric as Outer Layer and Carbon/Hycar 4501-Treated Inner Layer Before and After Exposure to Body Perspiration

		Resistance to HD vapor[a]							
		HD-vapor penetration, µg/cm²				HD-vapor retention, %			
	Add-on of carbon/ Hycar 4501,	Before exposure to body perspiration		After exposure to body perspiration		Before exposure to body perspiration		After exposure to body perspiration	
Inner layer material	oz/yd²	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr	0-2 hr	2-6 hr
Rayon nonwoven fabric	1.0	<0.1	<0.1	<0.1	0.5	>99.7	>99.8	>99.6	99.
Rayon nonwoven fabric	2.0	<0.1	0.2	<0.1	0.5	>99.6	99.5	>99.6	99.
Polyurethane foam/nylon fabric laminate	2.0	<0.1	<0.1	<0.1	<0.1	>99.6	>99.8	>99.6	>99.

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[a] Concentration of HD was 22.9 µg/l for 0-2 hr evaluation and 23.3 µg/l for 2-6 hr evaluation.

[b] Average values for three treated samples worn for 24 hours by three individuals. The inner layer was worn in contact with the skin.

b. Carbon tetrachloride capacity

The carbon tetrachloride capacities of samples of rayon nonwoven fabric and polyurethane foam/nylon fabric laminate identical to those described above were determined before and after exposure to body perspiration. These materials were worn for six working days. The CCl_4 capacities of the samples are given in Table III-21. It was concluded from these results that 2.0 oz/yd^2 of carbon/Hycar 4501 was more desirable for treating the rayon nonwoven fabric. The data indicate that the CCl_4 capacity of the treated foam was less affected by perspiration than was that of the treated nonwoven fabric. However, this would have to be confirmed by additional studies.

4. Evaluation of two-layer systems having various outer layers

Several two-layer systems with the rayon nonwoven fabric treated with carbon/Hycar 4501 as the inner layer and with various outer layers were evaluated for resistance to penetration by agents. The outer-layer materials were: (1) a 4.0-oz/yd^2 cotton sheeting treated to apply 4% Zepel B; (2) a 5.5-oz/yd^2 cotton poplin treated to apply 4% Zepel B; and (3) a 5.0-oz/yd^2 cotton-nylon oxford cloth treated to apply 4% Quarpel (Zepel B and Zelan AP). The 6.2-oz/yd^2 slack-mercerized cotton sheeting with 4% Zepel B, used as the outer layer in the 36 two-layer systems described in the previous section, was included in this series of tests. None of these two-layer systems was penetrated by HD, GB, or VX in the drop or expulsion tests.

Table III-22 gives the results of measurements of the resistance to penetration by vapor from radioactive liquid GB. The two-layer system with the Zepel B-treated mercerized cotton sheeting as the outer layer was slightly less resistant to GB vapor than the other systems. Drops of GB placed on the surface of the treated mercerized fabric were immediately absorbed, but the drops pearled on the other fabrics. This phenomenon probably accounts for the lower resistance to GB vapor of the mercerized sheeting.

[redacted]

Table III-21. Carbon Tetrachloride Capacities of Carbon/Hycar 4501-Treated Materials Before and After Exposure to Body Perspiration

Material	Add-on of carbon/ Hycar 4501, oz/yd^2	Carbon tetrachloride capacity[a] for 100 sq cm area, mg: Before exposure to body perspiration	Carbon tetrachloride capacity[a] for 100 sq cm area, mg: After exposure to body perspiration[b]
Rayon nonwoven fabric	1.0	6.3	3.0
Rayon nonwoven fabric	2.0	22.3	7.6
Polyurethane foam/ nylon fabric laminate	2.0	24.2	13.0

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[a] Concentration of CCl_4 was 5.4-5.5 mg/l and the flow rate was 1 l/min/100 cm^2.

[b] Average for three treated samples worn for 48 hours by three individuals.

[redacted]

Table III-22. Resistance of Two-Layer Systems to Penetration by Radioactive GB Vapor. Inner Layer of Rayon Nonwoven with Carbon/Hycar 4501 Treatment[a]

Outer layer	Weight of outer layer, oz/yd^2	Vapor penetration by GB[b]			
		µg		%	
		Outer layer	Both layers	Outer layer	Both layers
Cotton sheeting, 4% Zepel B	4.2	224	92	5.6	2.3
Mercerized cotton sheeting, 4% Zepel B	6.5	592	200	14.8	5.0
Cotton poplin, 4% Zepel B	5.7	286	72	7.2	1.8
Cotton-nylon oxford, 4% Quarpel	5.2	88	60	2.2	1.5

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[a] Treated to apply 1.0 oz/yd^2 of carbon/Hycar 4501 (5:1 solids ratio).

[b] Duration of test 6 hr at room temperature; 4 mg drop used.

5. Comparison of different binders for rayon nonwoven fabric for inner layer

As shown by the studies described above, a 2-oz/yd^2, rayon nonwoven fabric impregnated to apply 1-2 oz/yd^2 of carbon/Hycar 4501 (5:1 solids ratio) has good resistance to CW vapors. However, results of our previous work have shown that nonwoven fabrics treated with Hycar 4501 have poor tensile properties and abrasion resistance. Much better properties have been obtained in the past with Rhoplex HA-8 and with a mixture of Rhoplex B-15 and Rhonite 401 (5:1 ratio); hence, these materials were evaluated for use as binders in the rayon nonwoven fabric for the inner layer of CW-protection systems.

Samples of the nonwoven fabric were treated both from single baths and from separate baths to apply carbon in combination with Hycar 4501, Rhoplex HA-8, or the mixture of Rhoplex B-15 and Rhonite 401 as binders. The amounts applied were approximately 0.8 oz/yd^2 of the binder and 0.8 oz/yd^2 of carbon. When the carbon and binder were applied from separate baths, the fabric was padded first to apply 0.6 oz/yd^2 of the binder and then to apply 1.0 oz/yd^2 of a mixture of the binder and carbon in a 1:4 solids ratio. In all of these treatments, the solids ratio of carbon to binder was 1:1; whereas, the ratio of 5:1 was used in the previous studies of CW resistance.

The treated nonwoven fabrics were evaluated for resistance to HD vapor in two-layer systems with Zepel B-treated cotton fabric as the outer layer. The results, which are given in Table III-23, show that the HD-vapor retention of the systems was independent of the binder and the method of application. Increasing the binder-to-carbon ratio from 5:1 to 1:1 did not significantly affect the HD-vapor resistance, as can be seen by comparing the data in Tables III-14 and III-23.

As shown by the data in Table III-24, the nonwoven fabric treated with carbon and Rhoplex HA-8 from a single bath had poor tensile properties and poor abrasion resistance. On the basis of previous data no better physical properties were expected for the nonwoven fabric treated with the mixture of Rhoplex B-15 and Rhonite 401; therefore, the physical properties of this fabric were not determined. The results of these trials provided no basis for a choice among the three binders, but the nonwoven fabrics treated with these binders were all stiffer than desired. However,

[illegible]

[redacted]

Table III-23. HD-Vapor Resistance of Two-Layer Systems with Zepel B-Treated Cotton Fabric as Outer Layer and Nonwoven Fabric Treated with Carbon and Various Binders as Inner Layer

Treatment of inner layer[a]	HD-vapor penetration[b] µg/cm² 0-2 hr	HD-vapor penetration[b] µg/cm² 2-6 hr	HD-vapor retention,[b] % 0-2 hr	HD-vapor retention,[b] % 2-6 hr
Applied from single bath				
Carbon/Hycar 4501	0.2	1.8	99.2	96.7
Carbon/Rhoplex B-15/Rhonite 401[b]	<0.1	0.2	99.6	97.8
Carbon/Rhoplex HA-8	<0.1	1.2	99.6	99.6
Applied from separate baths				
Carbon/Hycar 4501	<0.1	0.3	>99.6	99.5
Carbon/Rhoplex B-15	<0.1	0.9	>99.6	98.4
Carbon/Rhoplex HA-8	<0.1	0.3	>99.6	99.5

---

[a] Padded to apply 0.8 oz/yd^2 of carbon and 0.8 oz/yd^2 of the latex binder.

[b] Concentration of HD was 22.2 µg/l for the 0-2 hr evaluation and 22.8 µg/l for the 2-6 hr evaluation.

[redacted]

[redacted]

Table III-24. Properties of Rayon Nonwoven Fabric Treated to Apply 1.6 oz/yd^2 of a Carbon/Rhoplex HA-8 Mixture[a]

Weight, oz/yd^2	3.6
Breaking strength, lb/in.	
Machine	10.4
Cross	12.7
Elongation at break, %	
Machine	10.2
Cross	9.7
Elmendorf tear, g	
Machine	853
Cross	1251
Abrasion resistance, cycles to rupture	
Dry	83
Wet	30
Air permeability, ft^3/min/ft^2, 0.5 in. water	16.5
Stiffness, mg	188

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[a] 1:1 solids ratio of carbon to Rhoplex HA-8.

[redacted]

a nonwoven fabric treated with a mixture of carbon/Hycar 2600X83 (an acrylic latex made by B. F. Goodrich) was not as stiff as the nonwoven fabrics treated with Rhoplex HA-8, Rhoplex B-15, or Hycar 4501. The Hycar 2600X83 did not adversely affect the carbon tetrachloride capacity of the carbon and was approved by the Project Officer for use in the plant production of the reinforced materials described in the next section.

V. PLANT PRODUCTION OF MATERIALS

It was concluded from the studies described in Section IV-C that the rayon nonwoven fabric and the polyurethane foam/nylon fabric laminate treated with a carbon/latex mixture had satisfactory resistance to CW vapor for use as the inner layer of a two-layer system. The Project Officer requested that plant production quantities of a scrim-reinforced nonwoven fabric and a polyurethane foam/nylon fabric laminate be prepared and treated with a carbon/latex mixture.

The reinforced nonwoven fabric was prepared and treated by The Kendall Company. Half of the nonwoven web was reinforced with scrim on one side of the nonwoven web and the other half was reinforced with scrim on both sides.

The reinforced polyurethane foam was prepared by Reeves Brothers and treated by The Kendall Company. Polyurethane foam with nylon tricot fabric flame-bonded to one side and an equal amount of nylon tricot fabric flame-bonded to both sides.

A. Nonwoven Fabrics

The Kendall Company of Walpole, Massachusetts, prepared approximately 1100 yards of carbon/Hycar 2600 X83-treated rayon nonwoven fabric reinforced with a nylon scrim. The rayon nonwoven web was prepared from $1\frac{9}{16}$-inch, 3.0-denier rayon [illegible] nylon scrim which was obtained from Southern Press and Filter Media Company was used for reinforcing the nonwoven fabric.

Initially an attempt was made to laminate the scrim to the nonwoven web with Rhoplex E-32 as the adhesive. However, difficulty was encountered in the plant because with existing equipment they could not keep the scrim sufficiently aligned with the nonwoven fabric. As a result, good adhesion between the scrim and the nonwoven fabric was not obtained.

Therefore, needle-punching was tried for bonding the scrim to the rayon nonwoven web. Half of the nonwoven web was reinforced by needle-punching with the scrim on one side of the nonwoven fabric and the other half was reinforced by needle-punching with scrim on both sides of the nonwoven web.

The reinforced nonwoven fabrics were then treated with a bath containing 2 parts activated carbon solids to 1 part Hycar 2600 X83 solids in an attempt to apply 2.4 oz/yd^2 of the carbon/Hycar solids. Trouble was experienced in maintaining a stable bath during the treatment and Kendall was not able to control the solids add-on as accurately as desired.

The treated reinforced nonwoven fabrics were shipped to the U. S. Army Natick Laboratories for in-house evaluations.

B. Polyurethane Foam/Nylon Fabric Laminate

Polyurethane foam with nylon tricot knit fabric flame-bonded to one side and an equal amount of polyurethane foam with nylon tricot fabric flame-bonded to both sides was prepared for us by Reeves Brothers at their Cornelius, North Carolina plant. The tricot knit fabric which was obtained from Guilford Mills weighed 2.1 oz/yd^2 and was flame-bonded to one side of a $\frac{3}{32}$-inch polyurethane foam and to both sides of $\frac{1}{8}$-inch foam. The thicker foam was used when flame-bonding to both sides to compensate for extra shrinkage so that the foam in both finished materials would be comparable in thickness.

The Kendall Company then attempted to treat both types of the reinforced polyurethane foam to apply 2.0 oz/yd^2 of carbon/Hycar 2600 X 83 (5:1 solids ratio).

The foam with the tricot knit nylon fabric laminated to both sides could not be treated. The material absorbed water preferentially from the bath causing a buildup of sludge in the bath. When the fabric came into contact with the sludge, it tended to stick causing uneven tension in the fabric. The uneven tension in the fabric caused it to slap against the drying cans, and the treated material was not recoverable in a useable form. As a result of these difficulties, Kendall discontinued attempts to treat the foam with the tricot fabric laminated to both sides. About 500 yards of the untreated polyurethane foam with nylon tricot knit laminated to both sides was shipped to the U. S. Army Natick Laboratories for in-house studies.

Although a similar problem was encountered during the treatment of the foam with the nylon tricot fabric laminated to one side only, it was possible to overcome part of the problem by putting the material through the bath with the foam side down so that it came into contact with the sludge. Controlling the web pickup was troublesome, and treatments of this material was stopped after about 300 yards had been treated. About 300 yards of polyurethane foam with tricot knit nylon fabric laminated to one side and treated with carbon/Hycar 2600 X 83 and about 200 yards of untreated material were supplied to the U. S. Army Natick Laboratories for in-house studies.

VI. PROTECTIVE GLOVES AND STRIPPABLE COATINGS FOR BOOTS

Three two-layer systems were evaluated as materials for protective gloves. The evaluation consisted of determination of the resistance to penetration by VX under simulated abrasive conditions. A 1 x 1 inch fabric sample was placed on a sheet of filter paper which rested on a horizontal glass plate. A 3- to 4-mg drop of VX was placed on the fabric. After 30 seconds, a metal weight that exerted a pressure of 1 psi was placed centrally on the drop of liquid and moved in circles to apply a grinding, abrasive action for 30 seconds. The weight was then left on the abraded area for 30 seconds.

The outer layer in each of the three two-layer systems was a Quarpel-treated, 5.0-oz/yd^2 cotton-nylon oxford cloth. The inner layers were: (1) a 1.4 oz/yd^2 rayon nonwoven fabric containing 5% Rhoplex B-15; (2) a 1.8-oz/yd^2 Fortisan fabric; and (3) a reinforced nylon-wood pulp paper (Experimental Paper No. 2-2-62). Each inner-layer fabric was sprayed on one side to apply 0.7 oz/yd^2 of S-330/Hycar 4501 solids.

Under the conditions of the test described, neither the oxford-Fortisan nor the oxford-paper system was penetrated by VX in eight tests. The oxford-rayon system was penetrated three times out of eight.

Three pairs of knit cotton gloves treated with XXC-3 by the U. S. Army Natick Laboratories were not penetrated by VX, GB, or HD in the standard drop and expulsion tests, although the material did absorb the agent drops. In tests for resistance to penetration by radioactive vapor, the gloves were penetrated by 0.5% of a 4-mg drop of VX in 24 hours, by 3.1% of a 4-mg drop of HD in 24 hours, and by 11.9% of a 4-mg drop of GB in 6 hours.

Two materials, Hycar 2671 and Rhoplex K-3, were tried as easily applied, strippable coatings to retard the penetration of leather boots by agents. Hycar 2671 was applied to shoe leather with a paint brush. At a thickness equivalent to 2.2 oz/yd^2, applied in several coats, the Hycar did form a strippable coating. By adding 1% of Carbopol to the Hycar, a strippable coating was obtained with a thickness equivalent to 1.4 oz/yd^2. The Carbopol improved the strippability of the coating, but the finish on the leather was pulled off with the coating. Rhoplex K-3, a soft acrylic resin, was applied with a brush to give coatings up to 3.6 oz/yd^2. It could not be removed from the leather and was very sticky even after drying for several days.

In accordance with a request of the Project Officer, no additional work was done for obtaining CW protection for boots or on the development of materials for protective gloves.

PART IV. STUDIES OF FLUOROCARBON COMPOUNDS

I. INTRODUCTION

As noted in Part I of this report, treatment with a fluorocarbon compound was the best method found for imparting liquid CW-agent repellency to candidate base materials for the expendable protective overgarment. In the early stages of the program, the fluorocarbon compounds then commercially available were evaluated for liquid CW-agent repellency, and it was found that 3M's FC-208 was the best available at that time for our use. However, we could not find a completely satisfactory flame retardant for use with FC-208 on our experimental nylon-cellulose papers and nonwoven fabrics treated with an acrylic binder, which was the best type of binder found for the materials. We also found that treatments with FC-208 had poor light stability. Therefore, studies were undertaken to prepare a new fluorocarbon oil and water repellent that would not have these disadvantages and also to prepare a fluorocarbon compound that would function as a flame retardant as well as an oil and water repellent.

Eleven new fluorocarbon compounds were synthesized and screened as oil and water repellents for cellulose materials and two new fluorocarbon compounds were synthesized and screened as both an oil and water repellent and a flame retardant. One of the chemicals was found to provide good oil- and water-repellent properties and was extensively evaluated.

Whatman No. 5 filter paper and an 80 x 80, desized and bleached, cotton sheeting weighing 3.3 oz/yd^2 were used in the screening studies, but only the sheeting was used in the extensive evaluations. The water repellency of treated samples was determined by contact angle measurements or by the standard ASTM Spray Test, and oil repellency was determined by contact angle measurements (with bis(2-ethylhexyl) hydrogen phosphite used as the oil) or by the 3M Oil Test.

II. SUMMARY AND CONCLUSIONS

The following eleven new fluorocarbon compounds were synthesized and evaluated as oil and water repellents for cotton: N-methylolperfluoropropylguanamine (VII), N-methylolperfluoroheptylguanamine (XVI), N-methylolperfluorocaprylurea (XVII), vinyl perfluorooctanoate (XVIII), 2,4,6-tris(hexadecafluorononyloxy)-s-triazine (XIX), 2,4-bis(hexadecafluorononyloxy)-6-chloro-s-triazine (XX), perfluoropropylamidomethylpyridinium chloride (XXI), perfluorobutylamidomethylpyridinium chloride (XXII), perfluorocaprylamidomethylpyridinium chloride (XXIII), hexadecafluorononylamidomethylpyridinium chloride (XXIV), eicosafluoro-1-undecanylamidomethylpyridinium chloride (XV). The reaction product of tetrakis(hydroxymethyl)phosphonium chloride with N-methylolperfluoropropylguanamine (XXVI), and the reaction product of tetrakis(hydroxymethyl)-phosphonium chloride with N-methylolperfluoroheptylguanamine (XXVII) were prepared and evaluated was water repellents, oil repellents, and flame retardants. Attempts to prepare tris(hexadecylfluorononyloxy)-antimony (XXVIII) for evaluation as a water repellent, an oil repellent, and a flame retardant were unsuccessful.

Compounds VII, XIX, XXI, XXII imparted neither oil nor water repellency to cotton; Compounds XVI, XVII, XVIII, XX imparted slight water repellency but no oil repellency; and Compounds XXIV and XXV imparted slight water and oil repellency. However, Compound XXIII was found to be a fair water repellent and an excellent oil repellent for cotton. Cotton fabric treated with Compounds XXVI and XXVII were flame retardant but were only slightly oil or water repellent.

Because of the encouraging results obtained with the perfluorocaprylamidomethylpyridinium chloride (Compound XXIII, abbreviated FCAMPC), it was evaluated extensively. The compound was found to impart some oil and water repellency to fabrics made from cellulose acetate, silk, nylon, Dacron, wool, and cotton; to leather, and to nylon-wood pulp and cellulose papers. It was especially effective on cotton fabric and cellulose paper.

A sample of a cotton fabric treated with this compound had better oil repellency than a sample of t[redacted] FC-208, both before and after 5 launderings. The FCAMPC-treated sample also had higher water repellency after the 5 launderings, but it had lower initial repellency. Accelerated weathering did not significantly change the breaking strength, water repellency, or oil repellency of an FCAMPC-treated cotton fabric; however, outdoor weathering caused about a 30% loss in water repellency. FC-208-treated cotton fabric behaved similarly, but lost all of its water repellency during comparable exposure to outdoor weathering.

The good laundry fastness of the FCAMPC treatment on cotton lead us to believe that reaction of the compound with the cotton had occurred, but it was found in later studies that the treatment had poor durability to dry cleaning and could be partially extracted with acetone. On the basis of this information, it appeared that the FCAMPC probably dimerized to a water-insoluble, organic solvent-soluble product rather than reacting with the cotton. However, this could not be substantiated, since attempts to prepare the dimer for characterization were unsuccessful.

The lowest add-on of FCAMPC at which maximum oil repellency was obtained on cotton fabric was 2%. The best conditions established for obtaining this add-on were these: pad-bath temperature and immersion time, about 50°C and 1-3 minutes; curing temperature and time, 110°C and 3 minutes; and drying temperature, 100°C. To avoid loss of fabric strength, it was necessary to use sodium acetate and urea with the FCAMPC. One part of sodium acetate, 0.3 part of urea, and 5 parts of FCAMPC was the best proportion found.

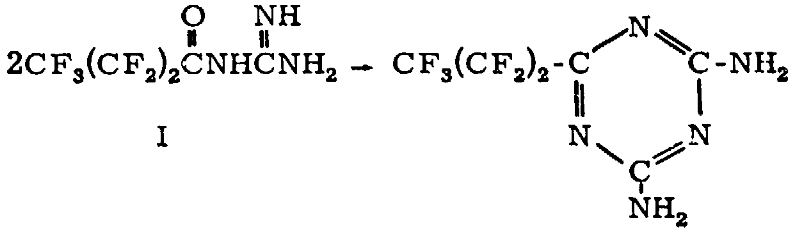
III. SCREENING STUDIES

A. Oil- and Water-Resistant Agents

1. N-Methylolperfluoroalkylguanamines

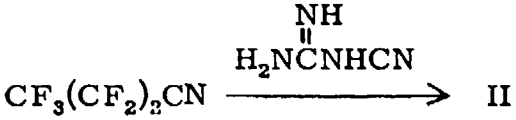
a. Propyl derivative

Perfluoropropylguanamine (II) was prepared by heating perfluorobutyrylguanidine (I) above its melting point and by treating perfluorobutyronitrile (III) with dicyandiamide.


I

II

(1)



$$CF_3(CF_2)_2CN \xrightarrow{H_2N\overset{NH}{\overset{\|}{C}}NHCN} II \qquad (2)$$

III

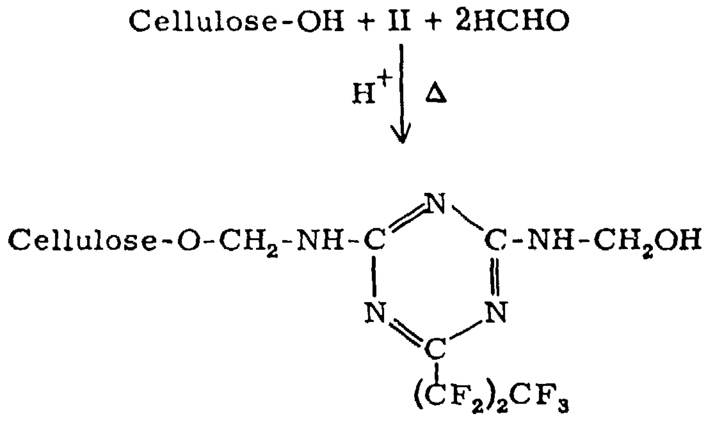
Compound I was prepared by the following series of reactions:

$$CF_3(CF_2)_2COOH \xrightarrow{CH_3OH} CF_3(CF_2)_2COOCH_3 \xrightarrow{H_2N\overset{NH}{\overset{\|}{C}}NH_2} I \qquad (3)$$

IV V

The oil- and water-repellent properties of perfluoropropylguanamine were evaluated by applying the compound to cotton fabric with formaldehyde and an acid catalyst and by measuring the oil and water repellency of the treated fabric. Formaldehyde and an acid catalyst were used with the guanamine in an attempt to carry out the reaction of the guanamine with the cellulose as shown below:

o-


VI

(4)

(1)

(2)

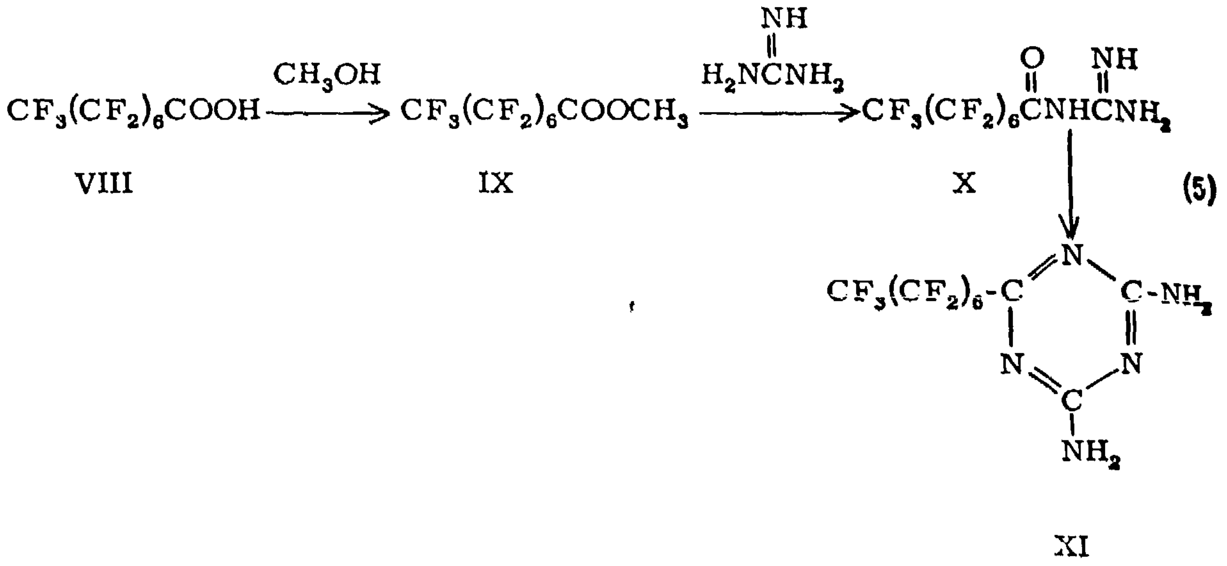
The results showed that II did not impart any oil or water repellency to the fabric at the 1.4% solids add-on at which it was evaluated. There are several possible reasons for this: the add-on was too low; the compound penetrated the fibers and did not provide the surface effect that is required to obtain oil and water repellency; the fluorocarbon moiety on the compound was too short; or the compound did not react with the cellulose or with itself to give insoluble products and, hence, was removed from the fabric during the washing operation that was part of the treatment. To investigate the latter possibility, a sample of perfluoropropylguanamine converted to a methylol derivative (VII) was applied to cotton fabric. Treatment of the fabric with this compound did achieve water repellency, but not oil repellency. To investigate the effect of a longer perfluoroalkyl group on oil and water repellency, perfluoroheptylguanamine was prepared and evaluated as described in the following section.

(3)

[redacted]

b. Heptyl derivative

Perfluoroheptylguanamine (XI) could not be prepared by the following reaction route:



(5)

The preparation was not successful under the conditions tried because perfluorocaprylurea, $CF_3(CF_2)_6\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NH_2$ (XII), was formed in the second step of the reaction instead of perfluorocaprylguanidine (X). Compound XI was prepared, however, by the reaction of perfluorocaprylonitrile with dicyandiamide, a reaction similar to (2). The perfluorocaprylonitrile was prepared from perfluorooctanoic acid by the following series of reactions:

$$\underset{}{VIII} \xrightarrow{SOCl_3} \underset{XIII}{CF_3(CF_2)_6COCl} \xrightarrow{NH_3} \underset{XIV}{CF_3(CF_2)_6CONH_2} \xrightarrow{P_2O_5} \underset{XV}{CF_3(CF_2)_6CN} \qquad (6)$$

An aqueous solution containing N-methylolperfluoroheptylguanamine (XVI) was prepared by treating XI with formaldehyde in the presence of a base, but it was not known whether the monomethylol or dimethylol

[redacted]

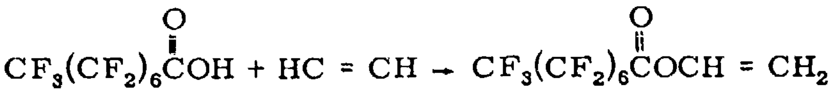
derivative was obtained. Samples of the 3.3-oz/yd^2, desized and bleached cotton fabric treated with this solution to apply 2.1% solids add-on had some water repellency, but there was only a very slight increase in oil repellency over that of an untreated fabric.

2. N-Methylolperfluorocaprylurea

Perfluorocaprylurea, prepared as indicated above, was treated with formaldehyde under acidic conditions to give N-methylolperfluorocaprylurea (XVII). Cotton fabric treated with this N-methylol derivative showed slight water repellency and no oil repellency.

3. Vinyl perfluorooctanoate

Vinyl perfluorooctanoate (XVIII) was prepared by the reaction of perfluorooctanoic acid and acetylene, and an attempt was made to graft copolymerize it with cotton cellulose.



$$CF_3(CF_2)_6\overset{O}{\overset{\|}{C}}OH + HC \equiv CH \rightarrow CF_3(CF_2)_6\overset{O}{\overset{\|}{C}}OCH = CH_2 \qquad (7)$$

XVIII

A sample of the bleached and desized cotton fabric was treated to apply 246% by weight of the vinyl compound, and the treated fabric was irradiated with 1 x 10^6 roentgens of gamma radiation from a cobalt-60 source. Under these conditions, the vinyl perfluorooctanoate underwent extensive homopolymerization, but only a small amount of the compound was grafted to the fabric. After the homopolymer had been extracted from the fabric, the fabric had some resistance to water but not to oil.

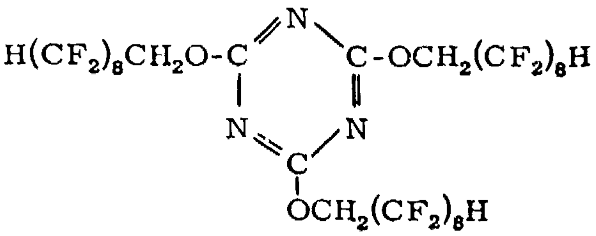
Graft copolymerization of vinyl perfluorooctanoate and cotton cellulose with gamma radiation in the presence of a solvent for the vinyl compound was also attempted. Two samples of the cotton fabric, one previously wet with water and the other dry, were immersed in an ethanol solution of vinyl perfluorooctanoate and irradiated with 1 x 10^6 roentgens of gamma radiation from a cobalt-60 source. Only a small amount of the vinyl compound was grafted to either sample. The treated samples showed slight resistance to water but none to oil.

When a sample of dry fabric immersed in an ethanol solution of vinyl perfluorooctanoate was irradiated with 5.3 x 10^6 roentgens of gamma radiation, a solids add-on of 3.4% was obtained, but the treated sample showed only slight resistance to water and none to oil.

4. Bis(hexadecafluorononyloxy)chlorotriazine

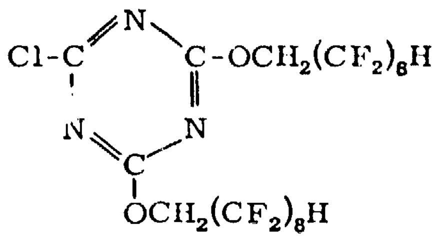
Cyanuric chloride appeared to hold promise as a means of binding fluorocarbon groups to cellulose and for contributing to flame resistance; consequently, the reaction products of cyanuric chloride and $HOCH_2(CF_2)_8H$ were investigated.

The reaction of the fluoroalcohol with cyanuric chloride can give mono-, di-, or tri-substituted triazines. In our initial studies, only the tri-substituted compound (XIX) was definitely identified as a reaction product of $HCF_2(CF_2)_7CH_2OH$ with cyanuric chloride. Since there is no chlorine available in this compound for reaction with hydroxyl groups of cellulose, no chemical attachment is likely. Filter paper treated with this compound was not water or oil repellent. This result indicates that, as surmised, a suitable fluoro-compound for providing the desired repellent properties, must contain some polar group that will cause it to be oriented on the surface of the cellulose [illegible] by forming a protective film.



XIX

2,4-Bis(hexadecafluorononyloxy)-6-chloro-*s*-triazine (XX) was prepared from cyanuric chloride and $H(CF_2)_8CH_2OH$.

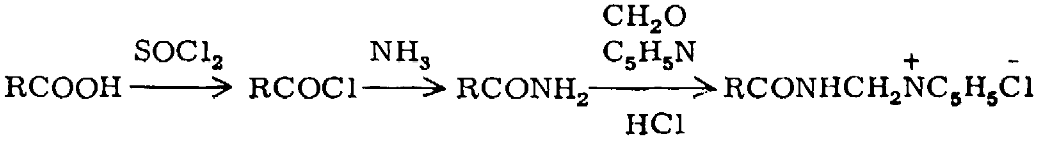


XX

Samples of filter paper treated with aqueous sodium hydroxide, then an ether solution of the triazine, and finally washed with water and dried had only a slight degree of water repellency. The poor water repellency was, probably, a result of the reaction of only a small quantity of the triazine with the paper under the conditions used.

5. Fluoroalkylamidomethylpyridinium chlorides

The following five fluoroalkylamidomethylpyridinium chlorides were prepared by the general reaction scheme shown in (8) and were evaluated as oil and water repellents for cotton fabric: perfluoropropylamidomethylpyridinium chloride (XXI), perfluorobutylamidomethylpyridinium chloride (XXII), perfluorocaprylamidomethylpyridinium chloride (XXIII), hexadecafluorononylamidomethylpyridinium chloride (XXIV), and eicosafluoro-1-undeconylamidomethylpyridinium chloride (XXV).



$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{NH_3} RCONH_2 \xrightarrow[HCl]{\substack{CH_2O \\ C_5H_5N}} RCONHCH_2\overset{+}{N}C_5H_5\overset{-}{Cl} \qquad (8)$$

$R = CF_3CF_2$-(XXI), $CF_3(CF_2)_2$-(XXII), $CF_3(CF_2)_6$-(XXIII),

$H(CF_2)_8$-(XXIV), $H(CF_2)_{10}$-(XXV)

The compounds were expected to react with cellulose in a manner similar to the alkyl pyridinium compounds that are widely used to produce laundry-fast, water-repellent effects on cotton textiles

$$\begin{array}{c}\text{Cellulose-OH} + \text{RCONHCH}_2\overset{+}{\text{N}}\text{C}_5\text{H}_5\overset{-}{\text{Cl}} \\ \downarrow \\ \text{Cellulose-O-CH}_2\text{NHOCR} + \text{C}_5\text{H}_5\text{N}\cdot\text{HCl}\end{array} \qquad (9)$$

The oil and water repellency of samples of the desized and bleached cotton fabric treated with Compounds XXI-XXV are summarized in Table IV-1. As shown by the results, the samples treated with Compounds XXIII, XXIV, and XXV had some oil and water repellency but those treated with Compounds XXI and XXII showed no resistance to either oil or water. The sample treated with Compound XXIII had slightly better water repellency and much better oil repellency properties than those treated with Compounds XXI or XXII.

B. Oil-, Water-, and Flame-Resistant Agents

1. N-Methylolperfluoroalkylguanamines-THPC condensates

Polymeric products of the perfluoroalkylguanamines (II and XI) and tetrakis(hydroxymethyl)phosphonium chloride (THPC), which are similar in structure to the melamine-THPC condensate that is widely used as a flame retardant for cellulose materials,[1] were investigated as oil-, water-, and flame-resistant agents.

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[1] W. A. Reeves and J. D. Guthrie, Ind. Eng. Chem. 48, 64 (1956).

Table IV-1. Oil- and Water-Repellent Properties of Cotton Fabric Treated with Fluoroalkylamidomethylpyridinium Chloride

Compound	Bath concn., %	Wet pickup, %	Add-on, %	Water repellency, spray ratings[a]	Oil repellency[b]
XXI	6.6	141	0.59	0	0
		126	0.52		
		126	0.43		
XXII	6.5	131	0.41	0	0
		127	0.53		
		122	0.54		
XXIII	8.0	-	2.0	70	130
		-	4.4	80	120
XXIV	8.0	131	2.1	50	50
		126	2.0	50	50
XXV	8.0	118	4.1	50	60
		123	2.8	50	60
		122	2.2	50	60

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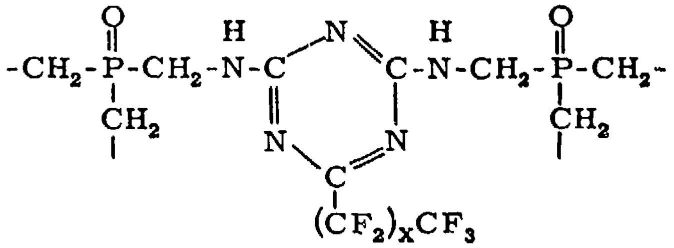
[a] By ASTM Method D 583-58, maximum water repellency = 100.

[b] By 3M Method, maximum oil repellency = 150.



XXVI and XXVII

XXVI (x = 2)
XXVII (x = 6)

a. Propyl derivative

A solution containing N-methylolperfluoropropylguanamine was prepared by treating perfluoropropylguanamine with formaldehyde under basic conditions. THPC was then reacted with the N-methylolperfluoropropylguanamine, and samples of the 3.3-oz/yd^2 cotton fabric were padded with the solution containing the reaction product (XXVI) to apply 38 to 40% solids add-on. The treated samples had fair water repellency, as determined by contact-angle measurements, and also had flame retardant properties, as determined by the match test. However, the treated samples did not have any oil repellency.

b. Heptyl derivative

This condensate (XXVII) was prepared by heating THPC with N-methylolperfluoroheptylguanamine, which was prepared by treating perfluoroheptylguanamine with formaldehyde under basic conditions. Samples of cotton fabric were padded with solutions of the reaction product to apply 3.4%, 16.4%, and 32.4% solids. The samples had a spray rating of 70 and an oil repellency rating of 50. Samples of the same cotton fabric treated to apply either 2.9% or 4.1% solids FC-208 had a spray rating of 90 and an oil repellency rating of 120.

The sample treated to apply 16.4% solids of the amine-THPC reaction product was consumed when evaluated by the match test. However, the sample treated to apply 32.4% solids had excellent flame resistance. After 5 launderings, it still had some resistance to water (spray rating of 50), but it had no resistance to oil, and it failed the match test.

2. Tris(hexadecylfluorononyloxy)antimony

Since mixtures of antimony oxide and halogenated paraffins are used extensively as flame retardants, it was reasoned that a compound containing antimony, oxygen, and a fluorocarbon moiety might function as an oil-, water-, and flame-resistant agent. Attempts were made to prepare tris(hexadecylfluorononyloxy)antimony (XXVIII) by the following reactions, but, because of hydrolytic instability and insolubility in organic solvents, the compound could not be isolated in pure form for evaluation.

$$Sb(OC_2H_5)_3 + 3HOCH_2(CF_2)_8H \rightarrow \underset{\text{XXVIII}}{Sb[OCH_2(CF_2)_8H]_3} \qquad (10)$$

$$Sb(OC_2H_5)_3 + 3NaOCH_2(CF_2)_8H \rightarrow \text{XXVIII}$$

IV. PERFLUOROCAPRYLAMIDOMETHYLPYRIDINIUM CHLORIDE

Because of the encouraging results obtained with perfluorocaprylamidomethylpyridinium chloride (FCAMPC, Compound XXIII), an extensive evaluation of the compound was carried out. Optimum conditions of application for obtaining maximum add-ons of FCAMPC on cotton fabric were sought, and the effect of the curing temperature on the properties of FCAMPC-treated cotton fabric was determined. The effect of the amount of FCAMPC on the oil repellency of cotton fabric was determined, and attempts were made to improve the water repellency and breaking strength of FCAMPC-treated cotton fabric. Various types of materials were treated with FCAMPC and evaluated for oil and water repellency, the effect of the FCAMPC treatment on the oil and water repellency of a cotton fabric was compared with the effects of some commercial fluorocarbon compounds, before and after laundering, dry cleaning, and weathering. The reaction of FCAMPC with cellulose was studied.

A. Basic Procedure of Applying FCAMPC

The basic procedure of applying FCAMPC used in these studies was to pad the materials with an aqueous bath containing 8% FCAMPC and 0.8% sodium acetate (10:1 weight ratio of FCAMPC to sodium acetate) at 45-50°C to apply 100% wet pickup. The padded samples were dried 3 minutes at 80°C and cured 3 minutes at 130°C. After curing, the samples were neutralized by treatment in a solution containing 0.1% of sodium carbonate and 0.25% of Lux liquid detergent at 60°C for 15 minutes. The neutralized samples were rinsed in water at 45-50°C for 1 hour and finally in cold water for 1 hour. The samples were dried at room temperature.

As a result of some of the studies described below, the following changes in the basic procedure were found to give markedly improved effects: changing the weight ratio of FCAMPC to sodium acetate to 5:1, immersing sample in the pad bath for 1-3 minutes prior to padding, lowering the curing temperature from 130 to 110°C, and increasing the final drying temperature to 100°C.

B. Effects of Conditions of Curing and Padding on Retention (Add-on) of FCAMPC by Cotton Fabric

The chemistry involved in the reaction of cellulose with a quaternary nitrogen compound, according to Mullin,[2] is as follows:

$$\begin{array}{l}
C_5H_5N(Cl)CH_2NH\text{-}CO\text{-}R \\
\quad\downarrow\ CH_3COONa \\
C_5H_5N(OOCCH_3)CH_2NH\text{-}CO\text{-}R \\
\quad\downarrow\ HOCell \\
C_5H_5N(OCell)CH_2NH\text{-}COR \\
\quad\downarrow\ \text{Heat} \\
RCO\text{-}NHCH_2OCell + C_5H_5N
\end{array} \qquad (11)$$

However, according to Zerner and Pollak[3] the reaction may involve the formation of the quaternary ammonium hydroxide as an intermediate and the following would happen:

$$\begin{array}{l}
ROCH_2\text{-}C_5H_5N\text{-}OOCCH_3 \\
\quad\downarrow\ H_2O \\
ROCH_2\text{-}C_5H_5N\text{-}OH \\
\quad\downarrow\ HOCell \\
ROCH_2\text{-}C_5H_5N\text{-}OCell \\
\quad\downarrow\ \text{Heat} \\
ROCH_2OCell + C_5H_5N
\end{array} \qquad (12)$$

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[2] C. Mullin, Textile Colorist 53, 834-837 (1931).

[3] E. Zerner and P. Pollak, Textile Research 14, 242-245 (1944).

Assuming either of these mechanisms of reaction to be correct, when FCAMPC reacts with cellulose under ideal conditions, approximately 80%, by weight, of the compound should remain attached to the cellulose and 20% should be lost as pyridine, or pyridine complexes.

The results of our initial studies revealed that the weight increase of cotton fabric after treatment with FCAMPC, curing, and neutralizing was much less than 80% of the amount applied. For example, the weight of a cotton fabric padded to apply 100% wet pickup of a 5% FCAMPC bath was increased only 0.3%, instead of the expected 4%, after it was cured 3.5 minutes at 150°C and neutralized and rinsed as described above. A similar treatment with a bath containing 25% FCAMPC (100% wet pickup) produced a weight increase of only 2.5% after curing, washing, and drying. Apparently, the reaction of the FCAMPC with the cellulose was incomplete under the conditions used and much of the fluorocarbon compound was lost during processing.

In efforts to make more effective use of FCAMPC, the effects of the following curing and padding conditions on the amount of FCAMPC retained by a 3.3-oz/yd^2 bleached and desized cotton fabric impregnated to apply 8% FCAMPC were determined: curing temperature, curing time, the ratio of FCAMPC to sodium acetate in the pad bath, pad-bath temperature, and the time of immersion of the sample in the pad bath. In these experiments, the basic procedure for treatment with FCAMPC described above was used, with the changes noted, except for variations in factors that were being studied. The amounts of FCAMPC retained by the treated samples under the various conditions of treatment were calculated from the increases in weights of the original samples (all conditioned at 21°C and 65% RH) and are expressed as percent add-on of FCAMPC. Results are given in Tables IV-2 through IV-6.

1. Curing temperature

Table IV-2 gives the add-ons of FCAMPC and repellencies of eight samples of the treated cotton fabric cured for 3.5 minutes at temperatures ranging from 56 to 177°C. Data on water and oil repellency are given for the samples before and after 5 launderings. For complete reaction, the theoretical add-on of the treated samples would have been 6.4%; the highest value found was 2.3%. In general, the add-on increased with

Table IV-2. Effect of Curing Temperature on Add-on and Repellent Properties of Cotton Fabric Treated with FCAMPC[a]

Curing temperature, °C	Add-on, % solids	Water repellency, spray rating[b]		Oil repellency[c]	
		Before laundering	After 5 laundering	Before laundering	After 5 laundering
56	2.2	0	0	130	0
82	1.8	50	0	120	0
93	2.3	70	0	120	50
110	1.1	70	70	120	100
130	1.9	70	70	110	90+
149	0.6	50	50	90	80
163	0.5	0	0	50	0
177	0.6	50	50	50	50

[redacted]

---

[a] 8% FCAMPC applied. Curing time was 3.5 minutes.

[b] Maximum water repellency = 100.

[c] Maximum oil repellency = 150.

Table IV-3. Effect of Curing Time at 110 and 130°C on Add-on of FCAMPC-Treated Cotton Fabric[a]

Curing conditions		
Temperature, °C	Time, minutes	Add-on, % solids
130	3	1.8
130	5	0.8
130	10	0.5
130	15	0.0
110	3	2.4
110	6	1.6

---

[a] 8% FCAMPC applied.

Table IV-4. Effect of Weight Ratio of FCAMPC to Sodium Acetate in Pad Bath on Add-on of FCAMPC[a]

Weight ratio of FCAMPC to sodium acetate	Add-on, % solids
1:0	3.3
20:1	3.2
10:1	3.6
5:1	3.3

---

[a] 8% FCAMPC applied. Samples cured at 110°C for 3 minutes.

Table IV-5. Effect of Pad-Bath Temperature on Add-on of FCAMPC[a]

Pad-bath temperature, °C	Add-on, % solids, at immersion times of < 1 minute
49	0.4
60	0.7
71	1.0
82	2.1

---

[a] Bath contained 8% FCAMPC, samples cured at 110°C for 3 minutes.

Table IV-6. Effect of Pad-Bath Immersion Time at 82°C and 50°C on Add-on of FCAMPC[a]

Temperature, °C	Time, minutes	Add-on, % solids
82	-[b]	2.1
82	3	5.3
82	4	4.8
82	7	9.7
50	-[b]	0.4
50	1	1.9
50	2	2.4
50	4	1.8

---

[a] Bath contained 8% FCAMPC, samples cured at 110°C for 3 minutes.

[b] About 0.5 minutes.

[redacted]

[redacted]

decreasing temperature of curing. The sample cured at 110°C had the best oil repellency (120) and spray rating (70) and had good durability to launderings. Therefore, it was concluded that the optimum curing temperature for cotton fabric treated with the perfluorocaprylamidomethylpyridinium chloride was 110°C.

2. Curing time

As shown in Table IV-3, the amounts of FCAMPC retained by samples of the treated cotton fabric cured at 110 or 130°C decreased with increased curing time. For example, a sample cured for 3 minutes at 110°C retained 2.4% of the 8% of FCAMPC applied, whereas a sample cured for 6 minutes at this temperature retained only 1.6% of the FCAMPC. A sample cured for 3 minutes at 130°C retained 1.8% of the 8% of FCAMPC applied, and a sample cured for 15 minutes at 130°C did not retain any. Thus it appears necessary to keep the curing time as short as possible.

3. Weight ratio of FCAMPC to sodium acetate

The effect of sodium acetate in the pad bath on the retention of FCAMPC by the fabric was investigated with baths containing weight ratios of FCAMPC to sodium acetate of 1:0, 20:1, 10:1, and 5:1. The average solids add-on of the samples was 3.4%; and as shown in Table IV-4, the add-on was independent of the weight ratio of FCAMPC to sodium acetate. The higher add-ons of these samples compared with those above (Tables IV-2 and 3) are attributed to longer immersion times in the pad bath.

4. Pad-bath temperature

To determine the effect of pad-bath temperature on the retention of FCAMPC by the cotton fabric, samples of the fabric were treated by padding with baths containing FCAMPC at temperatures ranging from 49 to 82°C. As shown in Table IV-5, when the samples were immersed in the pad baths for less than a minute (about 30 to 45 seconds) and immediately padded to apply 100% wet pickup, the add-ons of the samples after neutralization ranged from 0.4 to 2.1% and increased with increasing pad-bath temperature.

5. Pad-bath immersion time

To determine the effect of the time of immersion of a fabric sample in the pad bath on the retention of FCAMPC, samples were immersed in pad baths at 50 or 82°C for times ranging from less than 1 minute to 7 minutes and then they were padded to apply approximately 100% wet pickup. The add-ons of the cured and neutralized samples are shown in Table IV-6.

There was a general increase in the retention of FCAMPC by the fabric with increased immersion time in the pad bath. For example, 9.7% add-on was obtained for the sample immersed in the pad bath for 7 minutes, and a 2.1% add-on was obtained for the sample immersed in the pad bath for less than 1 minute. For complete reaction, the theoretical add-on of samples impregnated to apply 8% FCAMPC would be 6.4%. The add-on of 9.7% obtained with a bath-immersion time of 7 minutes indicates that the increase in add-on with an increase in bath-immersion time is due to an increase in exhaustion of the cationic FCAMPC onto the fabric.

With a pad-bath temperature of 50°C, there was a significant increase in the add-on of FCAMPC by the fabric when the immersion time was increased from about 0.5 to 1 minute; but longer immersion times gave no further increase in add-on.

C. Effect of Add-on of FCAMPC on Oil Repellency of Cotton Fabric

Samples of the 3.3-oz/yd^2 cotton fabric containing 0.4 to 5.3% FCAMPC were evaluated for oil repellency, and the results are shown in Figure IV-1. Each point in the graph is the average for 3 to 5 samples.

As shown in Figure IV-1, oil repellency increased to a maximum oil-repellency value of 130 and then it remained constant with increasing add-on of FCAMPC. The lowest add-on at which maximum oil repellency was obtained was about 2.0%.

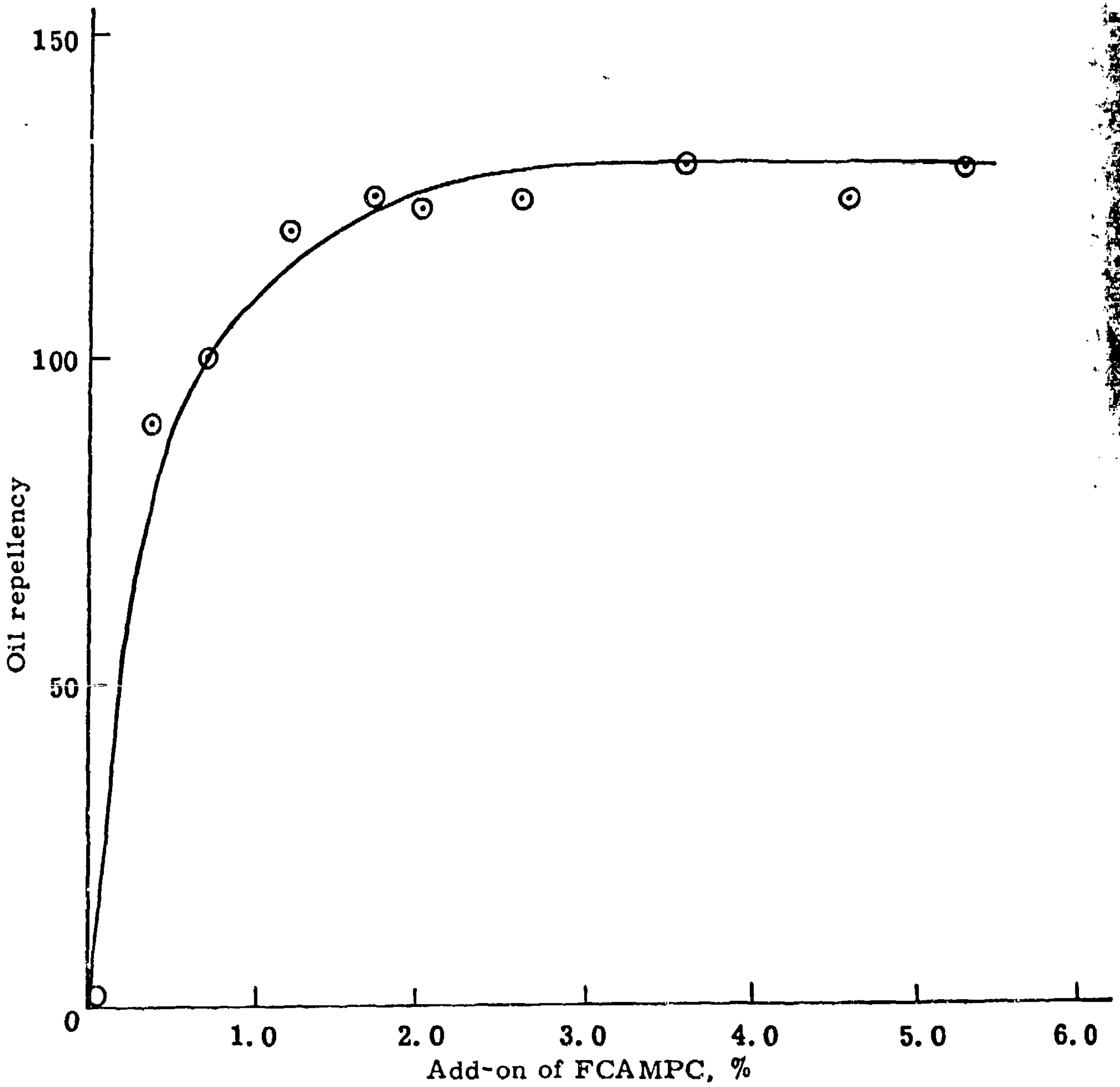

Figure IV-1. Relationship Between Add-on of FCAMPC and Oil Repellency Rating of FCAMPC-Treated Cotton Fabric (Samples cured at 110°C).

D. Attempts to Improve Properties of FCAMPC-Treated Cotton Fabric

1. Water repellency

The water repellencies of the FCAMPC-treated cotton fabrics that were prepared in the above studies were low — a spray-rating value of 70 was the highest value obtained. In attempts to improve water repellency, cured samples of the fabric were dried at 100°C after neutralization, rather than at room temperature. An investigation was also made of the desirability of using Zelan AP with FCAMPC. Zelan AP is a commercially available product containing an alkoxymethylpyridinium chloride that is widely used to produce laundry-fast water-repellent effects.

a. Increasing final drying temperature

Six samples of the 3.3-oz/yd^2 cotton fabric were treated with FCAMPC dried, cured, and then neutralized under similar conditions. After neutralization, three of the treated samples were dried at 20°C and the other three were dried at 100°C. The dried samples were evaluated for water repellency and for oil repellency. As shown in Table IV-7, there were no significant differences in the oil repellency of the samples dried at 20°C and of those dried at 100°C. However, all three of the samples dried at 100°C had higher spray ratings (80) than the three samples dried at 20°C (50-70).

b. Use of Zelan AP with FCAMPC

It was thought that improved water repellency might be obtained with FCAMPC by treating fabrics with a bath containing FCAMPC and a small amount of Zelan AP. Since the optimum curing temperatures for FCAMPC and Zelan AP are different, a cotton fabric treated with a mixture of the two compounds would have to be cured first at 110°C to cause the FCAMPC to react with the fabric and then cured at 160°C to cause the Zelan AP to react with the fabric. Therefore, a study was made to determine the effect of curing a FCAMPC-treated sample of the 3.3-oz/yd^2 cotton fabric first at 110°C for 3 minutes and then at 160°C for 3 minutes. After curing at 110°C, the dry, neutralized sample had an add-on of 1.3%; and it had an oil-rating value of 110 and a spray rating of 70. After

Table IV-7. Effects of Drying Temperature on Water and Oil-Repellency of FCAMPC-Treated Cotton Fabric

Drying temperature, °C	Add-on, % solids	Water repellency spray rating[a]	Oil repellency[b]
20	5.3	70	130
20	2.0	50	120
20	2.6	70	130
100	4.4	80	120
100	4.8	80	130
100	3.6	80	130

---

[a] Maximum water repellency = 100.

[b] Maximum oil repellency = 150.

recuring the sample at 160°C, the sample had no water or oil repellency. The weight of the sample indicated that all of the FCAMPC had been lost. From this study, it was concluded that Zelan AP could not be used effectively with FCAMPC to treat cotton fabrics.

2. Breaking strength

As shown in Table IV-8, treatment with FCAMPC alone caused a severe decrease in the breaking strength of the 3.3-oz/yd^2 cotton fabric; but addition of 1.6% sodium acetate to the pad bath containing 8% FCAMPC (weight ratio of FCAMPC to sodium acetate of 5:1) greatly reduced the loss in breaking strength, without adversely affecting water and oil repellency. The addition of 0.5, 1.0, or 2.0% urea to the pad bath containing 8% FCAMPC and 1.6% sodium acetate prevented any significant loss in the breaking strength of the treated cotton fabric. At the 0.5 and 1.0% concentration levels, the urea had only a slight effect, if any, on the water and oil repellencies of the treated samples; but, when 2.0% of urea was used, the treated sample had no water repellency, although it had excellent oil repellency.

In these studies, the samples of cotton fabric were padded with each bath to apply 100% wet pickup, and the padded samples were cured at 130°C for 3 minutes. After curing, the samples were neutralized and then redried at 100°C.

E. Water and Oil Repellency of Various Materials Treated with FCAMPC

The following materials were treated with FCAMPC and evaluated for water and oil repellency: 11.2-oz/yd^2 cellulose acetate fabric, 2.3-oz/yd^2 silk fabric, 2.1-oz/yd^2 nylon fabric, 2.5-oz/yd^2 Dacron fabric, 4.3-oz/yd^2 Dacron-cotton fabric, 8.2-oz/yd^2 polypropylene fabric, 7.8-oz/yd^2 wool fabric, 3.3-oz/yd^2 cotton fabric, leather, 2.5-oz/yd^2 50:50 nylon-wood pulp paper, and 2.5-oz/yd^2 all-cellulose paper.* All of the materials were treated by immersing a sample for several minutes in

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* Kaycel 100, an all-cellulose paper reinforced with 6 x 5 strands per inch of nylon yarn.

Table IV-8. Breaking Strength and Repellent Properties of FCAMPC-Treated Cotton Fabric

Composition of pad bath, %			Properties of cured samples[a]			
FCAMPC	Sodium acetate	Urea	Add-on, % solids	Breaking strength, lb	Spray rating[b]	Oil repellency
Untreated control			0	119	0	0
8	0	0	1.9	66	70	110
8	1.6	0	4.4	109	80	120
8	1.6	0.5	1.5	117	70	130
8	1.6	1.0	2.0	113	70	130
8	1.6	2.0	1.7	116	0	130

---

[a] Samples cured at 130°C for 3 minutes.

[b] Maximum water repellency = 100.

[c] Maximum oil repellency = 150.

an 8% aqueous dispersion of FCAMPC at room temperature, padding to apply 100% wet pickup, drying at 80°C for 3 minutes, curing at 110°C for 3 minutes, neutralizing, and then redrying at 100°C. The all-cellulose paper was immersed in the pad bath for 1 minute; the cotton, Dacron-cotton, and wool fabrics, and the nylon-wood pulp paper for 3 minutes; the leather and polypropylene fabric for 5 minutes; and the silk, nylon, cellulose acetate and Dacron fabrics for 10 minutes.

The add-ons and water- and oil-repellency ratings of the treated materials are shown in Table IV-9. The results show that some water repellency and oil repellency were imparted to all of the materials studied, except the polypropylene fabric which did not retain any FCAMPC. The treating conditions used were probably far from optimum for most of the materials, but these examples illustrate the wide range of materials to which FCAMPC can be applied to impart water and oil repellency.

F. Durability of FCAMPC Treatment to Laundering

Separate samples of a 3.3-oz/yd^2, desized and bleached cotton fabric were treated to apply 1.5 or 4.8% of FCAMPC, 4% of Quarpel, and 1.5 or 5.0% of FC-208. Separate samples of a scoured, 2.5-oz/yd^2 Dacron fabric were treated to apply 2.8% of FCAMPC or 3.7% of FC-208. The samples of treated cotton and treated Dacron were evaluated for water and oil repellency before and after 5 launderings. The results are given in Table IV-10.

Before laundering, the cotton samples treated with FCAMPC had lower water repellency but higher oil repellency than the FC-208 or the Quarpel-treated samples. After 5 launderings, the water repellency of the FCAMPC-treated cotton samples was better than the FC-208-treated samples but poorer than the Quarpel-treated samples. The cotton samples treated with the FCAMPC had better oil repellency after 5 launderings than the cotton samples treated with either of the other two products.

Before laundering, the Dacron sample treated with 2.8% FCAMPC had lower water repellency but slightly higher oil repellency than the FC-208-treated Dacron. After 5 launderings, the FCAMPC-treated Dacron still had slightly better oil repellency than the FC-208-treated Dacron, but both had equal water repellency.

Table IV-9. Water and Oil Repellency Ratings of Various Materials Treated with FCAMPC

Material	Add-on,[a] % solids	Water repellency, spray rating[b]	Oil repellency[c]
Cellulose acetate fabric	0.9	50	90
Silk fabric	1.0	50	90
Nylon fabric	0.1	50	120
Dacron fabric	2.0	50	90
Wool fabric	9.8	70	80
Cotton fabric	3.6	80	130
Dacron-cotton fabric	1.7	70	90
Leather	1.7	50	70
Polypropylene fabric	0.0	0	0
Nylon-wood pulp paper	<1.0	70	100
Cellulose paper	5.4	80	120

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[a] Determined by increase in weight after curing and neutralizing.

[b] Maximum water repellency = 100.

[c] Maximum oil repellency = 150.

Table IV-10. Water and Oil Repellency Ratings for Treated Cotton and Dacron Fabrics Before and After Laundering

Fabric	Treatment	Add-on, % solids	Water repellency, spray rating[a] Before laundering	Water repellency, spray rating[a] After 5 launderings	Oil repellency[b] Before laundering	Oil repellency[b] After 5 launderings
Cotton	FC-208	1.5	100	50	100	50
		5.0	90	50	120	80+
	Quarpel	4.0	100	100	110	80
	FCAMPC	1.5	70	70	110	90+
		4.8	80	70	130	110
Dacron	FC-208	3.7	100	50	90	80
	FCAMPC	2.8	50	50	90+	80+

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[a] By ASTM Method D 583-58, maximum water repellency = 100.

[b] By 3M Method, maximum oil repellency = 150.

G. Durability of FCAMPC Treatment to Dry Cleaning

Samples of a desized 3.3-oz/yd^2 cotton fabric were treated to apply 3.6% FCAMPC solids or 5.0% FC-208 and evaluated for water and oil repellency before and after 5 dry cleanings. The results are given in Table IV-11.

Before dry cleaning, the sample treated with 3.6% FCAMPC had a lower spray rating but higher oil repellency than the sample treated with FC-208; but after 5 dry cleanings, the sample treated with FC-208 had better oil repellency and a higher spray rating than the sample treated with FCAMPC.

H. Durability of FCAMPC Treatment to Weathering

1. Accelerated weathering

Separate samples of the 3.3-oz/yd^2, desized and bleached cotton fabric treated to apply 1.6% FC-208 solids or 1.8% FCAMPC solids were exposed for 26 hours in a Weather-Ometer. The breaking strength, water repellency, and oil repellency of each sample was determined before and after exposure; the results are given in Table IV-12.

The exposure in the Weather-Ometer did not affect the breaking strength or spray rating of either sample, but it decreased the oil repellency of the FC-208-treated sample. The oil repellency of the FCAMPC-treated sample was not affected by 26 hours in the Weather-Ometer.

2. Outdoor weathering

Separate samples of the 3.3-oz/yd^2 cotton fabric were treated to apply 4.5% FC-208 solids, 4.3% Zepel B solids, and 4% FCAMPC solids; and the treated samples were evaluated for water and oil repellency before and after outdoor weathering for 2 months. The results are given in Table IV-13.

Before outdoor weathering, the sample treated with FCAMPC had a lower spray rating than the samples treated with FC-208 or Zepel B. The sample treated with Zepel B had slightly better oil repellency than the

Table IV-11. Water- and Oil-Repellency Ratings of Treated Cotton Fabric Before and After Dry Cleaning

Treatment	Add-on, % solids	Water repellency, spray rating[a]		Oil repellency[b]	
		Before dry cleaning	After 5 dry cleanings	Before dry cleaning	After 5 dry cleanings
FC-208	5.0	90	70	120	100
FCAMPC	3.6	80	50	130	80

---

[a] By ASTM Method D 583-58, maximum water repellency = 100.

[b] By 3M Method, maximum oil repellency = 150.

Table IV-12. Effect of Accelerated Weathering on Breaking Strength and Repellent Properties of Treated Cotton Fabric[a]

Treatment	Add-on, % solids	Curing temperature,[b] °C	Exposure, hr	Breaking strength, lb/in.	Water repellency, spray rating[c]	Oil repellency[d]
None	0	-	0	112	0	0
None	0	-	26	91	0	0
FC-208	1.6	150	0	89	70	110
FC-208	1.6	150	26	88	70	90
FCAMPC	1.8	110	0	80	70	120
FCAMPC	1.8	110	26	79	70	120+

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[a] Fabrics were exposed in the Weather-Ometer for 26 hours at 52°C with cycles of 102 minutes of light and 18 minutes of spray.

[b] All samples were cured for 5 minutes.

[c] By ASTM Method D 583-58, maximum water repellency = 100.

[d] By 3M Method, maximum oil repellency = 150.

Table IV-13. Effect of Outdoor Weathering on Water and Oil Repellency Ratings of Treated Cotton Fabric[a]

Treatment	Add-on, % solids	Water repellency, spray rating[b]		Oil repellency[c]	
		Before weathering	After weathering	Before weathering	After weathering
FC-208	4.5	90	0	110	110
Zepel B	4.3	100	50	130	120
FCAMPC	4.6	70	50	120	120

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[a] Fabrics were exposed for 2 months (September-October 1963) on an outdoor weather board in Birmingham, Alabama.

[b] By ASTM Method D 583-58, maximum water repellency = 100.

[c] By 3M Method, maximum oil repellency = 150.

sample treated with FCAMPC which had slightly better oil repellency than the sample treated with FC-208. After outdoor weathering, the samples treated with Zepel B and FCAMPC had equivalent oil- and water-repellent ratings which were better than those for the FC-208-treated sample.

I. Reaction of FCAMPC with Cellulose

Studies were made to determine whether FCAMPC reacts with cellulose. A FCAMPC-treated cotton sample was extracted with acetone in an attempt to remove the FCAMPC, and studies were made to determine what reactions FCAMPC underwent when heated.

1. Extraction of FCAMPC-treated cotton fabric with acetone

A sample of a desized cotton fabric was treated to apply 3.0% of FCAMPC, and the treated sample was evaluated for water and oil repellency before and after extraction with acetone. The sample was extracted with acetone in a Soxhlet extractor for 96 hours, dried, and conditioned at 21°C, 65% RH. The weight loss and the water and oil repellent properties were determined. Then the sample was extracted with acetone for an additional 96 hours and evaluated again. The results are given in Table IV-14.

The extraction greatly decreased the oil repellency of the sample, but reduced the spray rating only to 50. These data indicate that only a small amount, if any, of the FCAMPC reacts with the cellulose under the conditions used for treatment.

2. Mechanism of decomposition of FCAMPC

Since extraction of an FCAMPC-treated cotton fabric indicated that little, if any, of the FCAMPC reacted with cellulose, studies were begun to determine if perhaps self condensation of FCAMPC occurred when it was heated. Self condensation could produce a dimer that would impart water and oil repellency when deposited on the fabric.

Table IV-14. Effect of Extraction with Acetone on FCAMPC-Treated Cotton Fabric

	Weight, g	Add-on, % solids	Water repellency, spray rating	Oil repellency
Initially[a]	4.7221	3.0	70	120
After 96 hours extraction	4.6523	1.2	50	50
After 192 hours extraction	4.6392	0.8	50	0

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[a] Sample weighed 4.5950 g before treatment.

Davis has reported[4] that cotton treated with steramidomethylpyridinium chloride by the conventional pad-dry-cure procedure contains some methylene steramide [$(C_{17}H_{35}CONH)_2CH_2$] and showed that this compound can also be formed by heating the pyridinium compound first in water and then in dilute acid:

$$C_{17}H_{35}CONHCH_2\overset{+}{N}C_5H_5\ \overset{-}{Cl} \xrightarrow[\text{heat}]{H_2O} C_{17}H_{35}CONHCH_2OH + C_5H_5NHCl \qquad (13)$$

$$2C_{17}H_{35}CONHCH_2OH \xrightarrow[\text{heat}]{H_2O + H^+} (C_{17}H_{35}CONH)_2CH_2 + HCHO + H_2O \qquad (14)$$

To determine whether FCAMPC undergoes self-condensation, FCAMPC was heated in a similar manner and the products were isolated and characterized.

An 8% solution of FCAMPC in water was boiled for 2 hours, and the yellow oil that formed was collected and solidified by cooling. The solid product was recrystallized twice from a hot benzene-ethanol solution (70:30 by volume) and then dried in a vacuum oven at 50°C. The recrystallized product melted at 95-95.5°C and had the correct elemental analysis and molecular weight for perfluorocaprylmethylolamide, the expected product.

<u>Calculated</u> for $C_9H_4F_{15}NO_2$: C, 24.38; H, 0.90; N, 3.16;
Mol. wt. 443.

<u>Found</u>: C, 24.28; H, 0.83; N, 3.30; Mol. wt. 430.

Several attempts were made to condense the perfluorocaprylmethylolamide in boiling 5% sulfuric acid, but a pure product could not be isolated from the reaction mixture. When a watch glass was placed over a beaker containing boiling sulfuric acid-perfluorocaprylmethylolamide solution, white crystals were deposited on the watch glass. These

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[4] F. V. Davis, J. Soc. Dyers and Colorists 63, 260-263 (1947).

crystals were insoluble in boiling water and melted at 114-116°C. It was thought that perhaps these crystals were the dimer, however, the elemental analysis and molecular weight of the crystals disproved this assumption. The crystals have not been identified, since there was not sufficient time remaining in the project to complete this portion of the work.

Calculated for $(C_7H_{15}CONH)_2CH_2$: C, 25.56; H, 0.67; N, 6.28;
Mol. wt. 892.

Found: C, 19.49; H, 0.52; N, 2.81; Mol. wt. 419.

V. EXPERIMENTAL DETAILS

A. Syntheses

1. N-Methylolperfluoropropylguanamine

Perfluoropropylguanamine was prepared by thermal cyclization of the corresponding guanidine compound, which was prepared from guanidine and methyl perfluorobutyrate, and by treatment of perfluorobutyronitrile with dicyandiamide. The N-methylol derivative of the guanamine was prepared by treating the guanamine with formaldehyde in the presence of a base.

a. Guanidine

A beaker containing 100 g of ethanol and 18 g of guanidine carbonate was placed in dry ice. When the mixture was cold, small beads of sodium were added slowly to it with stirring until 5 g of sodium had been added. The mixture was stirred continuously, and it was allowed to warm to room temperature. The mixture was then centrifuged, and the guanidine solution was decanted from the guanidine carbonate that had not reacted and the sodium carbonate that had formed. The guanidine solution was concentrated at reduced pressure.

b. Methyl perfluorobutyrate

Methyl perfluorobutyrate was prepared by esterification of the corresponding acid with methanol according to the procedure used by Burgoyne and Conden.[5]

Into a three-neck, round-bottom flask fitted with a reflux condenser, a thermometer, and a distilling receiver was put 10 g (0.05 mole) of perfluorobutyric acid, 2 g (0.06 mole) of methanol, and 2 g of chloroform. The mixture was heated at 56°C, and the water that formed during esterification was collected as an azetrope with the chloroform. When the amount of water collected approximated the theoretical yield, which took

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[5] E. E. Burgoyne and F. E. Conden, J. Am. Chem. Soc. 72, 3276 (1950).

less than 10 minutes, the reaction was considered complete; and the remainder of the reaction mixture was distilled. The methyl perfluorobutyrate was collected at 65°C.

The infrared spectrum of the product agreed with the infrared spectrum reported for methyl perfluorobutyrate.[6] The bands at 2970 cm^{-1} were characteristic of CH_3 stretching; the band at 1785 cm^{-1} showed C=O stretching. CF_3 stretching was shown at 1346 cm^{-1}; and the strong bands near 1200 cm^{-1} showed C-F stretching.

c. Perfluorobutyrylguanidine

Perfluorobutyrylguanidine was prepared according to the procedure used by Iwanza and Melsvhaski.[7] To a round-bottom flask fitted with a reflux condenser was added 5 g of methyl perfluorobutyrate and 5 g of the concentrated guanidine solution. A very mild exothermic reaction occurred immediately. The mixture was refluxed for 2 hours and then cooled to room temperature. After standing at room temperature for 36 hours, the white precipitate that formed was collected on a filter and washed several times with water. The melting point of the product was 166°C after purification. The infrared spectrum for the product showed no CH stretching. The following characteristic bands were observed, indicating that the perfluorobutyrylguanidine compound was formed.

$\gamma(cm^{-1})$	Assignment
3150-3550	N-H stretching bands
1680	Amide I (C=O stretching)
1640	C=N stretching
1614	NH_2 banding
1544	Amide II (secondary amine)
1348	CF_3 stretching
Near 1200	C-F stretching

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[6] R. N. Haszeldine and K. Leedham, "Documentation of Molecular Spectroscopy," Spectral Card No. 63 (1963).

[7] Namanckowa Iwanza and Yoshida Melsvhaski, <u>J. Pharm. Soc. Japan</u> <u>69</u>, 248 (1949).

d. Perfluoropropylguanamine from perfluorobutyrylguanidine

Perfluoropropylguanamine was prepared from perfluorobutyrylguanidine according to the procedure used by Simons and Weaver[8] for preparing alkylguanamines. The perfluoropropylguanamine was prepared by heating perfluorobutyrylguanidine in an open beaker at 10°C above its melting point (176°C) for 15 minutes. The product was recrystallized from hot water and dried in a desiccator. The melting point of this product, assumed to be perfluoropropylguanamine, was 220°C.

e. Perfluoropropylguanamine from perfluorobutyronitrile

Perfluoropropylguanamine was prepared from perfluorobutyronitrile and dicyandiamide by the procedure of Simons and Saxton.[9] To a flask fitted with a reflux condenser, a thermometer, and a stirrer, were added 1 g of potassium hydroxide dissolved in 20 ml of butyl Cellosolve and 4.2 g of dicyandiamide. The mixture was stirred continuously throughout the reaction period. Liquid heptafluorobutyronitrile, 10 g, was added and the mixture was heated at 170-180°C for approximately 20 minutes. Heating was then discontinued and the reaction mixture was allowed to cool during 2 hours. At the end of this time, the product was centrifuged, and the liquid portion was decanted from the solid material. The solid product was washed twice with water and then with acetone. The acetone-insoluble portion melted at 354°C, the melting point of melamine. The acetone-soluble portion was crystallized by cooling the solution and then recrystallized once more from acetone. The recrystallized product had a melting point of 199.5-202.0°C and elemental analysis indicated that it was probably impure perfluoropropylguanamine.

Calculated for $C_6H_4F_7N_5$: C, 25.82%; H, 1.43%; N, 25.09%

Found: C, 27.61%; H, 2.56%; N, 23.75%

The infrared spectrum of the compound indicated the presence of CF_2 and CF_3 groups.

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[8] J. K. Simons and W. I. Weaver (to Libby-Owens-Ford), U. S. Patent 2,408,694 (1946).

[9] J. Simons and M. Saxton, "Organic Syntheses," Vol. 33, 1st edition, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 13.

f. N-Methylolperfluoropropylguanamine

A solution that was expected to contain approximately 10% of N-methylolperfluoropropylguanamine was prepared by adding 1.39 g of perfluoropropylguanamine to a solution of 7.9 g of 38% aqueous formaldehyde in 4 ml of water at pH of 7-8. The mixture was heated to 70-80°C for 20 minutes and allowed to stand overnight at room temperature. The perfluoropropylguanamine dissolved on heating at 70-80°C and the solution remained clear after standing overnight.

2. N-Methylolperfluoroheptylguanamine

This compound was prepared by the reaction of perfluorocaprylonitrile with dicyandiamide and treatment of the product obtained with formaldehyde. Perfluorocaprylonitrile was prepared by treating perfluorocaprylamide with phosphorus pentoxide. The perfluorocaprylamide was prepared by the reaction of perfluorocapryl chloride with ammonia, and perfluorocapryl chloride was prepared by the reaction of perfluorooctanoic acid with thionyl chloride.

a. Perfluorocapryl chloride

To a 3-neck, round-bottom flask fitted with a reflux condenser and stirrer were added 100 g of perfluorooctanoic acid, 250 ml of thionyl chloride, and 1 g of pyridine. The mixture was refluxed for 22 hours, while being stirred, and then it was cooled to room temperature. The mixture was then poured into a separatory funnel, and the lower layer, which was assumed to be perfluorocapryl chloride, was drawn off.

b. Perfluorocaprylamide

The perfluorocapryl chloride prepared as described above was added during 2 hours to 400 ml of concentrated ammonium hydroxide, with continuous stirring. A white precipitate formed as the perfluorocapryl chloride was added to the ammonium hydroxide, and it was collected at the end of the reaction period by centrifuging the mixture and decanting the ammonium hydroxide. The precipitate was washed with water, and then dissolved in acetone. The solution was filtered, and the acetone was evaporated to yield 53.9 g of product after drying in a vacuum oven. The dry product melted at 142-145°C and had the correct carbon and nitrogen analysis for perfluorocaprylamide.

Calculated for $C_8H_2F_{15}NO$: C, 23.26%; N, 3.39%

Found: C, 23.9%; N, 3.55%

c. Perfluorocaprylonitrile

Several unsuccessful attempts were made to prepare and isolate perfluorocaprylonitrile by the dehydration of perfluorocaprylamide with phosphorus oxychloride, but dehydration of the amide to give the nitrile was successful only when phosphorus pentoxide was used as the dehydrating agent.

To a 3-neck, round-bottom flask fitted with a thermometer and a distilling apparatus was added 10 g of perfluorocaprylamide, 25 g of phosphorus pentoxide, and 40 ml of xylene. The mixture was stirred continuously while being heated. The product (6.2 g), which distilled at 110-115°C, was a clear, volatile liquid. The infrared spectrum of the product conformed to that expected for perfluorocaprylonitrile. The spectrum showed C≡N absorption near 2260 cm^{-1} and CF stretching near 1200 cm^{-1}. The elemental analysis of the product and the composition of perfluorocaprylonitrile are as follows:

Calculated for $C_8F_{15}N$: C, 24.30%; N, 3.54%

Found: C, 25.38%; N, 3.58%

d. Perfluoroheptylguanamine

To a 3-neck, round-bottom flask, fitted with a thermometer and a reflux condenser, was added 150 ml of butyl Cellosolve containing 2 g of potassium hydroxide (95%). Dicyandiamide, 4.2 g, and 19.6 g of perfluorocaprylonitrile were added to the solution. The mixture was rred continuously with a magnetic stirrer and heated at 170 to 180°C r 13 hours. The butyl Cellosolve was then decanted from the solid erial, and the product was washed with cool water, collected on a tted filter, and washed twice with warm water. The product, after ying in a vacuum desiccator, weighed 1.6 g and melted at 185 to 188°C. e infrared spectrum of the product showed the presence of CF_2 and CF_3 oups as well as NH_2 groups. The elemental analysis of the product gave rther evidence that it was perfluoroheptylguanamine.

Calculated for $C_{10}F_{15}H_4N_5$: C, 25.05%; N, 14.61%; H, 0.83%

Found: C, 25.43%; N, 14.91%; H, 1.28%

e. N-Methylolperfluoroheptylguanamine

A solution that was expected to contain approximately 5% of N-methylolperfluoroheptylguanamine was prepared by adding 0.6 g of perfluoroheptylguanamine to a solution of 2.07 g of aqueous formaldehyde (38%) in 15 ml of water at a pH of 7 to 8. The mixture was refluxed for 23 hours while being stirred continuously.

3. N-Methylolperfluorocaprylurea

Perfluorocaprylurea was prepared by treatment of methyl perfluorooctanoate with guanidine (in an attempt to prepare perfluorocaprylguanidine) and by treatment of perfluorocapryl chloride with urea by the method of Stoughton.[10] N-methylolperfluorocaprylurea was prepared by the reaction of perfluorocaprylurea with formaldehyde.

a. Methyl perfluorooctanoate

Methyl perfluorooctanoate was prepared by the same procedure used for preparing methyl perfluorobutyrate except that 10 g (0.024 mole) of perfluorooctanoic acid, 19 g of methanol (0.031 mole) and 1 g of

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[10] R. W. Stoughton, J. Org. Chem. 2, 514-521 (1938).

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chloroform were used. The reaction mixture was distilled and the meth perfluorooctanoate was collected in 63% yield at 159°C.

The spectrum of the product showed CH_3 stretching at 2970 cm^{-1} and 2860 cm^{-1}, C=O stretching at 1789 cm^{-1}, and C-F stretching near 1200 cm^{-1}. This spectrum was very similar to that obtained for methyl perfluorobutyrate and indicated that the product was methyl perfluorooctanoate.

b. Perfluorocapryl chloride

To a 3-neck, round-bottom flask fitted with a reflux condenser and stirrer were added 40 g of perfluorocaprylic acid, 80 ml of thionyl chloride, and 0.5 g of pyridine. The mixture was refluxed for 6 hours, while being stirred, and then it was cooled to room temperature. The mixture was poured into a separatory funnel, and the lower layer (31.1 g which was assumed to be perfluorocapryl chloride, was drawn off.

c. Perfluorocaprylurea from methyl perfluorooctanoate

To a round-bottom flask fitted with a reflux condenser was added 28 g of methyl perfluorooctanoate and the guanidine solution prepared above. The mixture was refluxed for 2 hours, and then allowed to stand without heating for 72 hours. At the end of the reaction period, a small amount of white crystals had formed. The reaction mixture was poured into 20 volumes of cold water and after 4 to 5 hours, a gel formed. The water was decanted and the residue was recrystallized from water, dried in a vacuum oven at 40°C (the material was extremely difficult to dry), and recrystallized from cold acetone to give 3.4 g of purified product, which melted at 188°C. Analysis of the product was in fair agreement with that calculated for perfluorocaprylurea.

Calculated for $C_9H_3F_{15}N_2O_2$: C, 23.68%; H, 0.66%; N, 6.14

Found: C, 22.93%; H, 0.97%; N, 5.96%

d. Perfluorocaprylurea from perfluorocapryl chloride

To a 200-ml, 3-neck flask fitted with a stirrer, reflux condenser, and dropping funnel were added 4.2 g of urea, 25 ml of benzene, and 2 drops of concentrated sulfuric acid. The solution was warmed and stirred while 3.1 g of perfluorocapryl chloride was added dropwise during 3 hours. This mixture was refluxed and stirred 1 hour, after addition was completed, and then cooled to room temperature. HCl gas was evolved during the reaction. The solid product was filtered off, washed with water, and dried in a vacuum desiccator. The dried product was washed with dilute aqueous sodium bicarbonate, then washed twice with water, and dissolved in acetone. The acetone solution was filtered, and the filtrate was cooled in an ice bath. The product that crystallized from the solution weighed 0.69 g, and melted at 175-185°C. Analysis indicated that it was the desired perfluorocaprylurea.

Calculated for $C_9H_3F_{15}N_2O_2$: C, 23.68%; H, 0.66%; N, 6.14%

Found: C, 23.76%; H, 0.99%; N, 6.29%

e. N-Methylolperfluorocaprylurea

The methylol derivative was prepared by a procedure used by Frick, Kottes, and Reid.[11] To 40 g of 35% aqueous formaldehyde solution was added 1.0 g of perfluorocaprylurea (2.1 x 10^{-3} mole) and 5 g of water. The solution was adjusted to a pH of 8 with sodium hydroxide solution and allowed to stand overnight at room temperature. This solution was designated Solution A.

The method described by Vail, Frick, Murphy, and Reid[12] was also used in an attempt to prepare N-methylolperfluorocaprylurea. To about 0.2 g of perfluorocaprylurea was added 2 ml of 38% aqueous formaldehyde solution and enough water to make 5 ml of solution. The mixture was

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[11] J. G. Frick, Jr., B. A. Kottes, and J. D. Reid, Textile Research J. 29, 314-321 (1959).

[12] S. L. Vail, J. G. Frick, Jr., Paul J. Murphy, and J. D. Reid, Am. Dyestuff Reporter 50, 200 (1961).

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adjusted to a pH of 8 with dilute sodium hydroxide solution and heated at 60°C for 20 minutes. The solution, designated Solution B, was then cooled to room temperature.

A third method used for preparing the methylol derivatives was as follows: To a 3-neck, round-bottom flask fitted with a reflux condenser and a thermometer was added 0.3 g of perfluorocaprylurea, 0.06 g of aqueous formaldehyde (38%), 20 ml of xylene, and approximately 0.001 g of toluenesulfonic acid. The mixture was stirred continuously with a magnetic stirrer and heated at 100-105°C. The mixture was kept at 100-105°C for 48 hours and then allowed to cool to room temperature and stand overnight. The precipitate that formed when the mixture cooled to room temperature was collected by filtration, washed with water, and dried in a vacuum desiccator. The yield was 0.11 g.

4. Vinyl perfluorooctanoate

Vinyl perfluorooctanoate was prepared by the reaction of acetylene and perfluorooctanoic acid, according to the procedure of Hawk and Jacobson.[13] The vinyl perfluorooctanoate and a cotton fabric were graft copolymerized with the aid of gamma radiation.

a. Preparation of vinyl perfluorooctanoate

The reaction was carried out in a 3-neck, round-bottom flask fitted with a thermometer; a condenser, which was connected to a trap immersed in a dry ice-acetone bath; and a gas distributor inlet. Perfluorooctanoic acid (50 g), red mercuric oxide (3 g), hydroquinone (0.2 g), and mercuric sulfate (3 g) were added to the flask. The mercuric sulfate was prepared by allowing a mixture of 11 g of mercuric oxide and 5 g of sulfuric acid to stand overnight. The mixture was heated to 60-70°C, and then

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[13] B. W. Hawk and R. A. Jacobson (to Du Pont), U. S. Patent 2,436,144 (1948).

purified acetylene was bubbled through the mixture. The mixture was stirred continuously with a magnetic stirrer while the acetylene was being added. The acetylene was purified by passing it through water, solid caustic soda, solid calcium chloride, and a trap immersed in a dry ice-acetone bath.

The temperature of the mixture was gradually raised during a 40-minute period to 90-95°C, and, after 3 hours at this temperature, an additional 1 g of red mercuric oxide and an additional 1 g of mercuric sulfate were added. The mixture was kept at 90-95°C for an additional 2 hours, and then allowed to cool to room temperature and stand overnight. The mixture was then vacuum distilled into a container immersed in a dry ice-acetone bath and the distillate was treated with a small amount of sodium bicarbonate. After standing for 3 days, the distillate was redistilled, and the product (12.4 g) boiling at 161-165°C was collected. The refractive index of the product (n_D^{20}) was 1.3160. The infrared spectrum for the product conformed to that expected for vinyl perfluorooctanoate. The spectrum showed C=O stretching at 1790 cm^{-1}, C=C stretching at 1652 cm^{-1}, and 890 cm^{-1}, and CF stretching near 1200 cm^{-1}.

b. Graft copolymerization of vinyl perfluorooctanoate and cotton cellulose in absence of solvent

A bleached and desized cotton fabric weighing 3.3 oz/yd^2 was used for this study. A sample that weighed 0.3986 g at 65% RH and 21°C was immersed in undiluted vinyl perfluorooctanoate, and then it was put through the Butterworth Padder to apply 246% wet pickup. The impregnated sample was placed in a glass test tube, and the tube was placed in an aluminum container fitted with a bellows valve. After capping the container, it was alternately evacuated to a pressure of approximately 1 mm of Hg and flushed with nitrogen 5 times. The container was then sealed while filled with nitrogen and placed in the center of a cobalt-60 radiation source. After receiving 1 x 10^6 roentgens of gamma radiation, the irradiated sample was removed from the source and washed for 10 minutes with acetone and then 2 hours with running water to remove the homopolymer. Before washing, a large amount of homopolymer was attached to the surface of the sample. After being conditioned at 65% RH and 21°C, the sample weighed 0.4028 g, indicating that a maximum of only 1% of vinyl perfluorooctanoate was grafted to the cellulose.

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c. Graft copolymerization of vinyl perfluorooctanoate and cotton cellulose in presence of solvent

An alcohol solution of vinyl perfluorooctanoate was prepared by mixing 6 g of ethanol with 6 g of vinyl perfluorooctanoate. Six grams of the alcohol solution was put into each of two test tubes. A sample (No. 1) of the 3.3-oz/yd^2 cotton fabric that weighed 0.2171 g (conditioned weight, 21°C-65% RH) was placed in one of the test tubes. Another sample (No. 2) of the cotton fabric that weighed 0.2779 g (conditioned weight) was wet with distilled water to a total weight of 0.53 g. The wet sample was put into the second test tube.

The test tubes containing samples were placed in an aluminum container fitted with a bellows valve. The container was capped, alternately evacuated to a pressure of approximately 1 mm of Hg and filled with nitrogen 5 times. The container was sealed while filled with nitrogen and placed in the center of a cobalt-60 radiation source. After receiving 1 x 10^6 roentgens of gamma radiation, the irradiated samples were removed from the source, washed 10 minutes with acetone, and 2 hours with running water to remove the homopolymer. The samples were then dried at 65% RH and 21°C.

After drying, Sample No. 1 weighed 0.2200 g, indicating that there was a maximum add-on of 1.3% solids. Sample No. 2, which was irradiated in the presence of water, weighed 0.2808 g. Therefore, the maximum solids add-on for Sample No. 2 was only 1%.

Neither sample showed any oil repellency as determined by placing a drop of bis(2-ethylhexyl) hydrogen phosphite on the surface of the material. A drop of water pearled on Sample 1, but penetrated the fabric in approximately 3 minutes. A water drop also pearled on Sample 2, but penetrated the sample in less than 1 minute.

A sample of a 3.3-oz/yd^2, bleached and desized cotton fabric that weighed 0.3231 g (conditioned weight, 21°C and 65% RH) was placed in a test tube containing a solution of 3 g of vinyl perfluorooctanoate in 3 g of ethanol. The test tube containing the sample was placed in an aluminum container fitted with a bellows valve. After capping, the container was alternately evacuated to a pressure of approximately 1 mm of Hg and filled with nitrogen 5 times. The container was then sealed while filled with nitrogen and placed in the center of a cobalt-60 radiation source. After receiving 5.3 x 10^6 roentgens of gamma radiation, the irradiated samples were removed from the container and washed 30 minutes with acetone and 2 hours with running water to remove the homopolymer. The sample was then dried at 65% RH and 21°C.

After being dried, the sample weighed 0.3242 g, indicating that there was a maximum add-on of 3.4% solids. Drops of water placed on the surface of the sample pearled initially, but were absorbed in 1 to 5 minutes, depending on the location of the drop on the sample. Evidently the fluorocarbon was not applied uniformly.

5. Hexadecafluorononyloxychlorotriazines

A tri-substituted triazine, 2,4,6-tris(hexadecafluorononyloxy)-s-triazine, was obtained from the reaction of the sodium salt of the C_9 fluoroalcohol, $H(CF_2)_8CH_2OH$, and cyanuric chloride in attempts to prepare either the mono- or di-substituted triazine. A di-substituted triazine, 2,4-bis(hexadecafluorononyloxy)-6-chloro-s-triazine, was obtained, however, by reacting the C_9 fluoroalcohol, rather than its sodium salt, with cyanuric chloride. The preparations of these triazine compounds are described below.

a. 2,4,6-Tris(hexadecafluorononyloxy)-s-triazine

The following method based on procedures patented by Ciba[14, 15] was used:

The C_9 fluoroalcohol (4.32 g, 0.010 mole) was placed in a round-bottom flask and heated to 50°C. Sodium (0.24 g, 0.010 mole) was added over a period of 10-15 minutes while the mixture was stirred continuously. Ten to fifteen minutes after addition of the sodium was completed, 10 ml of acetone was added to the flask, followed by 3.0 g (0.016 mole) of cyanuric chloride in 10 ml of acetone. On addition of the cyanuric chloride, the temperature rose to 50°C. The mixture was stirred for an hour at room temperature, and then kept for 48 hours at room temperature. The precipitate that formed was filtered off, washed with water,

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14. Ciba, Swiss Patent 106,116 (1924).
15. Ciba, Swiss Patent 106,407 (1924).

air dried, and then recrystallized from boiling carbon tetrachloride. The recrystallized product was washed with cold carbon tetrachloride and dr in a vacuum desiccator. This product was recrystallized from boiling heptane, and dried in a vacuum oven at 60°C, to yield 2.03 g of product, which melted at 106-107°C. The product gave a negative test for chlorine, indicating that tri-substitution had occurred to give 2,4,6-tris(hexadecanonyloxy)-s-triazine. The infrared spectrum of the product agreed with the infrared spectra for other tri-substituted triazines.[16] The band at 800 cm^{-1} was characteristic of the triazine ring, the bands at 1150 cm^{-1} were characteristic of CF_2 stretching, and the band at 1200 cm^{-1} was characteristic of ring plus CF_2 stretching.

Other reactions were carried out with the same procedure, but at reaction temperatures of 0° and 60°C. The tri-substituted derivative was obtained from all the preparations. When the amount of C_9 fluoroalcohol used in the reaction was decreased in an attempt to decrease the chance of forming the tri-substituted compound, it was again obtained.

b. 2,4-Bis(hexadecafluorononyloxy)-6-chloro-s-triazine

2,4-Bis(hexadecafluorononyloxy)-s-triazine was prepared by the reaction of cyanuric chloride with $H(CF_2)_8CH_2OH$ in the following manner: To 80 ml of acetone in an Erlenmeyer flask was added 17.28 g (0.04 mole) of the fluoroalcohol. While the mixture was stirred at room temperature, 6.0 g (0.056 mole) of sodium carbonate in 100 ml of water was added. Finally, 8.20 g (0.044 mole) of cyanuric chloride in 80 ml of acetone was slowly added to the mixture during 1 hour. After the mixture had been stirred for 24 hours at room temperature, the precipitate that had formed (presumably sodium chloride) was filtered off with a fritted-glass funnel, and the filtrate was allowed to stand overnight at room temperature. The filtrate, which had separated into two layers on standing, was placed in a separatory funnel and the lower layer was drawn off into an evaporating dish. After evaporation was complete, a gel remained. The upper layer of the filtrate was poured into 4000 ml of water. A gel precipitated after 2-3 hours. The water was decanted and the gel was dried. The pro

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[16] W. N. Padgett, III, and W. F. Hamner, J. Am. Chem. Soc. 8, 803 (1958).

ined from both layers of the filtrate were dissolved together in ether, d the insoluble residue was filtered off. The ether was evaporated from e filtrate and the product was dried in a vacuum desiccator to yield 10 g 44% yield) of a product melting at 84-86°C. Analysis indicated that it was e desired product, 2,4-bis(hexadecafluorononyloxy)-6-chloro-s-triazine.

Calculated for $C_{21}H_6N_3F_{32}ClO_2$: C, 25.7%; H, 0.61%; N, 4.31%

Found: C, 24.66%; H, 0.95%; N, 4.24%

6. Perfluorocaprylamidomethylpyridinium chloride (FCAMPC)

Throughout the investigation of FCAMPC, improvements were made the procedures used for preparing it, and the details of the best procedures developed are given below. The FCAMPC was prepared by the reaction of perfluorocaprylamide with pyridine by the method used by rth and Deese[17] for preparing alkylamidomethylpyridinium chlorides. The perfluorocaprylamide was prepared by the reaction of perfluorocapryl chloride with ammonia, and the perfluorocapryl chloride was prepared by the reaction of perfluorooctanoic acid with thionyl chloride.

a. Perfluorocapryl chloride

To a 3-neck, round-bottom flask fitted with a reflux condenser and stirrer were added 85 g of perfluorooctanoic acid, 195 g of thionyl chloride, and 1 ml of pyridine. The mixture was refluxed for 36 hours, while being stirred, and then it was cooled to room temperature. The cooled mixture was poured into a separatory funnel, and the lower layer of perfluorocapryl chloride was separated. The yield of perfluorocapryl chloride was 70 g (78.5%).

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[17] W. V. Wirth and R. F. Deese, Jr. (to Du Pont), U. S. Patent 2,291,519 (1942).

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b. Perfluorocaprylamide

The 70 g of perfluorocapryl chloride prepared as described above was added during 4 hours to 600 ml of concentrated ammonium hydroxide, with continuous stirring. A white precipitate formed as the perfluorocapry chloride was added to the ammonium hydroxide. At the end of the reactio period, the ammonium hydroxide was decanted from the mixture, and the white precipitate of perfluorocaprylamide was washed three times with 800-ml portions of water by centrifuging the mixture and decanting the water. The yield of perfluorocaprylamide after drying in a vacuum oven at 40°C for 24 hours was 62 g (92.8%). The product melted at 142-145°C and had a satisfactory carbon and nitrogen analysis for perfluorocaprylamide.

Calculated for $C_8H_2F_{15}NO$: C, 23.26%; N, 3.39%

Found: C, 23.9%; N, 3.55%

c. FCAMPC

To a 3-neck, round-bottom flask fitted with a reflux condenser and a thermometer were added 62.0 g of the perfluorocaprylamide, 13.0 g of paraformaldehyde, 0.25 g of p-toluenesulfonic acid, and 1200 ml of benzene. The mixture was refluxed while being stirred vigorously. After the mixture had refluxed for 40 hours, 15.5 g of pyridine and 5 ml of 2-butanone were added. After 2 hours additional reflux, about 750 ml of the benzene was distilled from the mixture and 900 ml of xylene was added. Refluxing, with stirring, was continued for an additional 40 hours, and then hydrogen chloride was bubbled through the refluxing solution for the next 6 hours. Two hours after completion of the addition of the hydrogen chloride, additional pyridine was added in small quantities until the solution was neutral to litmus paper. Heating was then terminated. As the mixture cooled, a yellow-brown, waxy material precipitated from the reaction mixture. While the solution was still warm, it was poured into a separatory funnel, and the waxy material was collected and dried.

The dried product was extracted with hot acetone, leaving a dark oil that was discarded. The acetone solution was evaporated to dryness, and the tan-colored, waxy residue was washed three times with boiling n-heptane and then dried in a vacuum oven at 40°C for 28 hours to give 54 g of product, which corresponds to a 66.5% yield of perfluorocaprylamidomethylpyridinium chloride.

The infrared spectrum of the product corresponded to the spectrum expected for perfluorocaprylamidomethylpyridinium chloride, but the product did not have the correct elemental analysis for perfluorocaprylamidomethylpyridinium chloride, and attempts at further purification were unsuccessful.

Calculated for $C_{14}F_{15}H_8O\overset{+}{N}\overset{-}{Cl}$: C, 31.1%; H, 1.49%; N, 5.18%; Cl^- 6.56%

Found: C, 33.2%; H, 2.45%; N, 6.15%; Cl^- 9.10%

An attempt was made to obtain some indication of the purity of the product by comparisons of the amounts of titratable acid and ionic chlorine present in the product with the amounts of these materials present in pyridine hydrochloride, the expected principal impurity in FCAMPC. Titrations were carried out potentiometrically with 0.1 N NaOH for the determination of acid and with 0.1 N $AgNO_3$ for the determination of chloride, and the results obtained are given in Table IV-15 with the calculated theoretical values for the pure compounds. Assuming that pyridine hydrochloride was the only impurity present in the sample of FCAMPC, it is possible to calculate from the data on milliequivalents (meq) of titratable acid per gram that the sample contained approximately 85% FCAMPC. This value is in reasonable agreement with the value of 89.6% calculated from the data on meq of titratable chlorine per gram.

7. Perfluorocaprylamidomethylmorpholinium chloride

An unsuccessful attempt was made to prepare perfluorocaprylamidomethylmorpholinium chloride following the procedure for perfluorocaprylamidomethylpyridinium chloride as described above with morpholine substituted for pyridine in the reaction [illegible]

Table IV-15. Titratable Acid and Chlorine Present in FCAMPC and Related Materials

	Titratable acid, meq/g		Titratable chloride, meq/g	
Compound	Found	Calculated	Found	Calculated
Pyridine hydrochloride	8.730	8.734	-	8.744
FCAMPC	2.883	1.849	2.567	1.850

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[a] End point at pH 9.

6. Perfluoropropyl and perfluorobutylamidomethylpyridinium chlorides

These compounds were prepared from perfluoropropionamide and perfluorobutyramide and purified by the procedures described above for preparing and purifying FCAMPC. The yields and elemental analyses of the products obtained are given below.

Propyl derivative

Yield: 26.3%

Calculated for $C_9F_5H_8O\overset{+}{N}\overset{-}{Cl}$: C, 37.2%; H, 3.85%; N, 9.64%; $\overset{-}{Cl}$, 12.2%

Found: C, 38.1%; H, 3.11%; N, 11.3%; $\overset{-}{Cl}$, 10.6%

Butyl derivative

Yield: 51.9%

Calculated for $C_{10}F_7H_8O\overset{+}{N}\overset{-}{Cl}$: C, 35.3%; H, 2.37%; N, 8.23%; $\overset{-}{Cl}$, 10.4%

Found: C, 35.1%; H, 2.81%; N, 9.09%; $\overset{-}{Cl}$, 10.9%

A sample of the propyl derivative yielded 2.904 milliequivalents of titratable acid per gram and contained 10.6% of titratable chloride. The theoretical values for the pure derivative are 3.441 milliequivalents of acid per gram and 12.2% chloride. Therefore, assuming no other titratable material present, the purity of the product based on milliequivalents of titratable acid was 84.4%. Since the chloride content of the product was low, it would seem that the impurity contains no titratable chloride and the purity on this basis was 86.9%. This does not preclude the possibility that some impurity consists of equivalent amounts of pyridinium hydrochloride and the methylol derivative of pentafluoropropionamide.

On the bases of the milliequivalents of titratable acid per gram (3.405) and the percent ionic chloride content (10.9%), the butyl derivative was 91.9-97.6% pure.

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9. Hexadecafluorononylamidomethylpyridinium chloride

a. Hexadecafluorononanoic acid

Hexadecafluorononanoic acid was prepared from hexadecafluorononyl alcohol by the procedure described by Berry.[18]

Seventy-two grams of hexadecafluorononyl alcohol, which had been purified by recrystallization from hot chloroform, and 500 ml of glacial acetic acid were heated to 100°C in a 2-liter, 3-neck, round-bottom flask fitted with two reflux condensers and a thermometer. The reaction mixture was stirred vigorously by means of a magnetic stirrer. Sixty grams of finely ground potassium permanganate was added over a 2-hour period to the reaction mixture through one of the condensers. The temperature of the reaction mixture varied between 90 and 105°C during the addition. After the addition of permanganate was completed, the reaction mixture was refluxed for 2 hours at 110°C, cooled to room temperature, and sulfur dioxide gas was added, while it was stirred vigorously, until all the manganese dioxide had been reduced. The acetic acid was then removed from the mixture by distillation at reduced pressure with a water aspirator. Attempts at removing the final traces of acetic acid from the crude manganese salt by repeated codistillations with toluene were not completely successful.

The crude manganese salt after drying at 45-50°C in a vacuum oven for 48 hours was converted to the hexadecafluorononanoic acid by mixing it with 42% sulfuric acid and extracting the mixture with ethyl ether to remove the acid. Since acetic acid is infinitely soluble in ethyl ether, some of it was extracted along with the desired product. This was confirmed by the acetic acid odor of the product obtained after evaporation of the ether. The ether-extractable material was further purified by recrystallizing it from xylene solution (65 g), cooled to 5-10°C in an ice bath. The white, crystalline material that precipitated from the xylene was collected and dried for 16 hours at room temperature in a vacuum oven. The dried material had a m.p. of 50-52°C and represented a 63% yield.

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[18] K. L. Berry (to Du Pont), U. S. Patent 2,559,629 (1948).

b. Hexadecafluorononylamide

The amide was prepared by converting the hexadecafluorononanoic acid to acid chloride with thionyl chloride and reacting the acid chloride with ammonium hydroxide, as described above for the conversion of perfluorooctanoic acid to perfluorocaprylamide. A total of 94 g of hexadecafluorononanoic acid was converted to 33.7 g (37% yield) of hexadecafluorononylamide having a m.p. 140-141°C.

c. Hexadecafluorononylamidomethylpyridinium chloride

The procedure described above for the preparation of perfluorocaprylamidomethylpyridinium chloride was followed, and 22.7 g of a yellow, waxy paste was obtained from 33.7 g of the hexadecafluorononylamide. The ionic chloride content of the product was 10.8%. Since the theoretical ionic chloride is 6.19%, contamination with some impurity with a higher ionic chloride content than the product was indicated. Treatment of the product with acetone lowered the ionic chloride content to 7.76%, but repetition of the acetone treatment caused no further decrease. The final product was a yellow wax whose elemental analysis was 32.37% C, 2.02% H, 6.06% N, and 7.76% Cl. The theoretical analysis of the desired product is 31.5% C, 1.58% H, 4.89% N, and 6.19% Cl.

10. Eicosafluoro-1-undecanylamidomethylpyridinium chloride

a. Eicosafluoro-1-undecanoic acid

Eicosafluoro-1-undecanoic acid was prepared from eicosafluoro-1-undecanyl alcohol in the same manner as the hexadecafluorononanoic acid. Sixty-eight grams of product (m.p. 105-106°C) was obtained from 81 g of alcohol. The yield was 83%.

b. Eicosafluoro-1-undecanamide

Eighty-eight grams of eicosafluoro-1-undecanoic acid was converted to the amide in the same manner as the perfluorooctanoic acid (page 363). The yield was 42.9 g (49%) of the amide (m.p. 150-152°C).

c. Eicosafluoro-1-undecanylamidomethylpyridinium chloride

The 42.9 g of the amide of eicosafluoro-1-undecanoic acid was treated in the same way as the amide of perfluorooctanoic acid (page 363). A yellow waxy product which weighed 19.6 g was obtained. The ionic chloride content of the product was 11.3% and the theoretical for the desired product is 5.27%. An attempt to remove the Cl impurity responsible for the high chlorine content in the same manner that the perfluorobutyrylam methylpyridinium chloride product was purified did not succeed. The ionic chloride content of the acetone soluble material was 12.9%. The elemental analysis of the acetone soluble material was 6.79% N, 38.17% C, 3.75% H, and 12.9% Cl^-. The theoretical values for eicosafluoro-1-1-undecanylamidomethylpyridinium chloride are 4.17% N, 30.35% C, 1.35% H, and 5.27% Cl^-.

11. Fluoroalkoxymethylpyridinium chloride

Two unsuccessful attempts were made to prepare eicosafluoroun methylpyridinium chloride, $H(CF_2)_{10}CH_2OCH_2N^+C_5H_5Cl^-$, by the procedure described in U. S. Patent 2,277,174[19] for the synthesis of alkoxymethylpyridinium chloride compounds.

12. N-Methylolperfluoropropylguanamine-THPC condensate

A solution that was expected to contain approximately 10% of N-methylolperfluoropropylguanamine was prepared by adding 1.39 g of perfluoropropylguanamine to a solution of 0.8 g of 38% aqueous formaldehyde in 4 ml of water at a pH of 7 to 8. The solution was heated for 20 minutes at 70 to 80°C, 2.0 g of THPC was then added, and the mixture was heated approximately 10 minutes at 60 to 70°C. At the end of this period, the mixture was quite viscous.

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[19] E. Waitman (to Heberlein Patent Corporation), U. S. Patent 2,277,174 (1942).

The solution was divided into two parts — one part was boiled gently on a hot plate until polymerization proceeded to the point where the entire product was a hard mass. The second part was used for treatment of a cotton fabric as described in Section V-B-6.

The hard mass obtained by heating was kept in boiling water for 30 minutes, and then washed in acetone for 10 minutes. The infrared spectrum of the product showed OH absorption near 3400 cm^{-1}; NH absorption near 3250 cm^{-1}; aliphatic CH at 2950 cm^{-1}; and CF absorption in the 1200 cm^{-1} region. Phosphorus also absorbs in the 1200 cm^{-1} region, and it is possible that some of the absorption in this region can be attributed to the phosphorus in the compound. The compound contained 13.3% nitrogen and 6.9% phosphorus as determined by elemental analysis, as compared to 16.2% nitrogen and 7.2% phosphorus calculated for a 1:1 reaction product of the N-methylol derivative and THPC.

13. N-Methylolperfluoroheptylguanamine-THPC condensate

To a 3-neck, round-bottom flask fitted with a reflux condenser was added 4.8 g of perfluoroheptylguanamine, 1.7 g of formaldehyde (38% aqueous solution), and 27.0 g of water. The solution was adjusted to pH 7-8. The mixture was heated and stirred for 18 hours, but all of the guanamine had not dissolved so an additional 6.2 g of formaldehyde solution was added. At the end of 4 hours additional heating, a reddish brown material had precipitated. The water was then decanted, and the gummy material was dried in the vacuum desiccator to give 3.4 g of product. The infrared spectrum of the product resembled the spectrum of perfluoropropylguanamine, but also indicated that the product might have been the methylol derivative.

To a round-bottom flask fitted with a reflux condenser and thermometer was added 2.6 g of the recovered material in 20.9 g of ethanol, and 2.0 g of THPC in 9.2 g of water. The pH of the solution was slightly greater than 6. The solution was heated with stirring for 1.5 hour at 60-70°C, and then used for the treatment of a cotton fabric as described in Section V-B-7.

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14. Tris(hexadecafluorononyloxy)antimony

a. Antimony triethoxide

A procedure of Meerwein and Bersin[20] was followed for preparing antimony triethoxide. To 400 ml of ethanol was added 14.4 g (0.63 mole) of metallic sodium. The mixture was stirred until all of the metal had reacted. Then a solution of 45.7 g (0.2 mole) of antimony trichloride dissolved in 140 ml of ethanol was slowly dropped into the sodium ethoxide solution. A precipitate of sodium chloride formed immediately. The addition was made over a period of about 1 hour. The reaction flask was then fitted with a condenser, and excess ethanol was distilled off. Antimony triethoxide was next distilled from the residual salt at 95-100°C[21] and 11 mm Hg pressure. Antimony triethoxide is a clear liquid that fumes in air and is very readily decomposed by water.

b. Tris(hexadecafluorononyloxy)antimony

To 45 ml of toluene was added 2.6 g (0.01 mole) of antimony triethoxide, 13.0 g (0.03 mole) of $H(CF_2)_8CH_2OH$, and 3 or 4 crystals of benzenesulfonic acid to serve as a catalyst. The antimony triethoxide was soluble in toluene, but it produced a slight cloudiness in the mixture. After the solution had refluxed slowly for an hour, a white, milky phase separated from the solution. The solution was distilled, and 1.10 g of a liquid that distilled 79-80°C (presumably ethanol from the ester exchange) was collected. The toluene was then distilled off.

The distillation residue was washed with toluene, the wash mixture was centrifuged, and the toluene was decanted. This procedure was repated three times. The product was placed in a vacuum desiccator and dried. The product decomposed at 286-290°C without melting. Analysis showed that the expected product, $Sb[OCH_2(CF_2)_8H]_3$, was not obtained. The product may have been a mixture of $Sb(OEt)_3$ and $Sb[OCH_2(CF_2)_8H]_3$.

Calculated for $C_{27}H_9F_{48}SbO_3$: C, 22.9%; H, 0.6%; Sb, 8.6%

Found: C, 16.52%; H, 1.01%; Sb, 7.0%

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[20] H. Meerwein and T. Bersin, J. Physical Chem. 39, 1125-1133 (1935).

[21] Literature value of Meerwein and Bersin was 95.5°C at this pressure.

B. Methods of Treatment with Repellents

1. N-Methylolperfluoropropylguanamine

$Zn(NO_3)_2 \cdot 6H_2O$, 0.7 g, dissolved in 1 ml of water, was added to a 10% solution of N-methylolperfluoropropylguanamine (V-A-1-f) to serve as catalyst and the solution was applied to a 3.3-oz/yd^2 cotton fabric by padding to leave 100% wet pick-up. The impregnated fabric was dried 7 minutes at 60°C and cured 3 minutes at 160°C. After curing, the fabric was rinsed first with acetone, then with water, and finally it was dried at room temperature.

The treated fabric was tested with a drop of water and the contact angles were 86° after 1 minute and 78° after 5 minutes, indicating some water repellency.

2. N-Methylolperfluoroheptylguanamine

Two grams of zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, dissolved in 2 ml of water was added to a 5% solution of N-methylolperfluoroheptylguanamine (V-A-2-e) to serve as a catalyst. A bleached and desized cotton fabric weighing 3.3 oz/yd^2 was padded with the solution to apply 155% wet pickup. The padded samples were dried 7 minutes at 60°C and cured 3 minutes at 160°C. After curing, the samples were washed with acetone for 2 hours, and with water for 2 hours, and then were dried at 21°C and 65% RH. The average solids add-on was 2.1%, as determined by the increase in weight of the treated samples conditioned at 21°C and 65% RH.

Drops of water were placed on the treated fabric; and the contact angles were 117° after 1 minute and 111° after 5 minutes, indicating reasonably good water repellency. The treated fabric showed only a slight increase in resistance to bis(2-ethylhexyl) hydrogen phosphite compared to the untreated fabric.

3. N-Methylolperfluorocaprylurea

Solution A of methylolperfluorocaprylurea (V-A-3-e) was diluted with enough water to make a solution containing approximately 5% solids. Then 0.5% of zinc nitrate (predissolved) on total weight of bath was added to the solution. Samples of Whatman No. 5 filter paper were dipped in the solution and put through a Butterworth padder to apply a wet pickup of 225%. The impregnated samples were dried and cured at 60°C for 7 minutes or at 160°C for 3 minutes. The cured samples were washed with acetone, air dried, and then washed in running water for 2 hours. The papers so treated were not water repellent nor oil repellent, as shown by the immediate penetration of a drop of water and of a drop of bis(2-ethylhexyl) hydrogen phosphite. Nitrogen was determined on an air-dried sample of the treated paper by a Kjeldahl method described by Cole and Park.[22] The treated sample contained less than 0.1% nitrogen, which was the limit of sensitivity of the method. The low nitrogen content indicated that chemical reaction of the methylol derivative and paper had not occurred to a significant extent.

Solution B of N-methylolperfluorocaprylurea (V-A-3-e) was cooled to room temperature, and a crystal of $Zn(NO_3)_2 \cdot 6H_2O$ was added. A piece of filter paper was immersed in this solution for 3 minutes, and the treated paper was dried for 10 minutes at 135°C. The treated paper was instantly penetrated by a drop of water.

A solution was prepared by adding 0.1 g of the N-methylolperfluorocaprylurea solid prepared above (V-A-3-e) to 0.9 g of acetone. Then approximately 0.05 g of $Zn(NO_3)_2 \cdot 6H_2O$ was added to the solution. A sample of 3.3 oz/yd^2, bleached and desized cotton fabric that weighed 0.128 g at 65% RH and 21°C was immersed in the N-methylolperfluorocaprylurea solution, put through the Butterworth padder to removed excess solution, and dried in a circulating oven at 140°C for 15 minutes. The dried sample was washed 10 minutes in acetone and 1.5 hours in water and dried at 65% RH and 21°C. The dried sample weighed 0.149 g at 65% RH and 21°C, indicating a 0.021-g increase in weight or a 16.4% solids add-on. A drop of water placed on the treated cotton fabric pearled, but it was absorbed in 4 minutes. The CW agent simulant, bis(2-ethylhexyl) hydrogen phosphite, penetrated the fabric instantly.

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[22] J. D. Cole and C. R. Parks, Ind. Eng. Chem., Anal. Edition 18, 61 (1946).

Alkaline solutions of perfluorocaprylurea and formaldehyde were heated at different temperatures in attempts to prepare N-methylolperfluorocaprylurea, and the solutions were used in the presence of an acid catalyst to treat cotton fabric. Three different solutions were made by adding 1 part of perfluorocaprylurea to 2 parts of aqueous formaldehyde (38%) and 16.6 parts of water. Enough sodium hydroxide solution was added to each solution to adjust the pH to between 7 and 8. One solution was heated at 80-90°C for 20 minutes and cooled to room temperature. The second solution was heated at 80-90°C for 20 minutes, cooled to room temperature, and allowed to stand for 24 hours. The third solution was boiled for 20 minutes (water being added at intervals to replace that evaporated) and cooled to room temperature. To each of these solutions was then added 0.6 part of $Zn(NO_3)_2 \cdot 6H_2O$ dissolved in 3 parts of water. Samples of 3.3-oz/yd^2 cotton fabric were padded with each of the solutions to apply approximately 100% wet pickup. The treated samples were dried 7 minutes at 60°C, cured 3 minutes at 160°C, washed in acetone, washed in water, and finally dried at room temperature. None of the samples was oil or water repellent.

4. Hexadecafluorononyloxytriazines

a. 2,4,6-Tris(hexadecafluorononyloxy)-s-triazine

2,4,6-Tris(hexadecafluorononyloxy)-s-triazine (V-A-5-a) was evaluated as a water and oil repellent for paper. Whatman No. 5 filter papers were impregnated with a 5% solution of the triazine in xylene. The solution was kept warm during the treatment to prevent precipitation of the solids. The papers were dipped in the solution and then put through the Butterworth padder to apply an approximate wet pickup of 200%.

Contact angles of water drops were measured to evaluate the water repellency. The water drop on the paper treated with the triazine had a contact angle of 42° after it had been on the paper 1 minute and it was absorbed at 3.5 minutes. In comparison, a water drop on paper treated with 2% FC-208 solids had a contact angle of 96° after it had been on the sample 1 minute and 94° after 5 minutes. Bis(2-ethylhexyl) hydrogen phosphite, a compound considered to be typical of oils, penetrated the paper treated with triazine in 10 seconds. These results indicate that the compound was not effective as a water or oil repellent.

b. 2,4-Bis(hexadecafluorononyloxy)-6-chloro-s-triazine

The attempted reaction of 2,4-bis(hexadecafluorononyloxy)-6-chloro-s-triazine (V-A-5-b) with the cellulose in paper to impart oil and water repellency was carried out basically by the method of Warren, Reid, and Hamalainen[23] for the reaction of cyanuric chloride with cellulose. The method involved treatment of the cellulose with alkali, removal of excess alkali, and subsequent treatment of the alkali-treated paper with the triazine.

Pieces of Whatman No. 5 filter paper were soaked for 5 minutes in 14% aqueous sodium hydroxide and then put through the Butterworth padder to remove excess solution. The average wet pickup of alkali was 223%.

Samples of the alkali-treated paper were immersed for 1 hour in a solution of 20 ml of ether containing an amount of the triazine equivalent to the weight of the untreated paper. The treated paper was air dried, rinsed successively with ether and with acetone, washed for 2 hours with running water, and air dried. Controls were prepared in the same manner, except that the triazine was not added to the ether. The triazine-treated paper had no water repellency.

Nitrogen was determined on air-dried samples of the treated paper by a modified Kjeldahl method described by Cole and Parks.[22] The treated samples contained less than 0.1% nitrogen (the lower limit of sensitivity of the method), in contrast to an expected nitrogen content of about 1% if quantitative chemical reaction of the triazine and the cellulose in the paper had occurred.

An attempted reaction of the triazine with the cellulose in paper was carried out by a modification of the above method. To a flask fitted with a reflux condenser was added 0.4 g of the triazine and 21 ml of ether. A piece of filter paper which had been dipped in dilute sodium hydroxide solution was added to the flask, and the solution was refluxed 1.5 hours. The liquid was decanted and the paper was dried at room temperature. A drop of water penetrated the treated paper immediately.

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[23] J. Warren, J. D. Reid, and C. Hamalainen, Textile Research J. 2 584-586 (1952).

In another experiment, alkali-treated filter paper (0.65 g) was placed in a hot solution (135°C) of 20 ml of xylene and 0.65 g of the triazine. After 10 minutes, the paper was removed from the solution, dried at room temperature, washed with ether and water, and then it was dried at room temperature. A control sample of paper was treated in the same manner, except that the triazine was not added to the xylene. Drops of water placed on the treated paper pearled, but the control paper was penetrated immediately. The contact angles of the drops on the treated paper were 86° after 1 minute and 75° after 5 minutes. The same treatment was applied to a 3.3-oz/yd^2 cotton fabric. The contact angles of water drops on the treated fabric were 67° after 1 minute and 50° after 5 minutes. Thus, water repellency was imparted to the treated paper and fabric. However, a drop of bis(2-ethylhexyl) hydrogen phosphite placed on the fabric to check the oil repellency penetrated immediately.

5. Perfluoroalkylamidomethylpyridinium chloride

a. Perfluorocaprylamidomethylpyridinium chloride

Cotton fabric treated with FCAMPC (V-A-6) was found to have excellent oil repellency and fair water repellency. The best procedure found for treatment of 3.3-oz/yd^2 cotton fabric with FCAMPC was to immerse the fabric in an aqueous bath containing 8% of the compound and 1.6% of anhydrous sodium acetate (5:1 weight ratio of FCAMPC to sodium acetate) at 43-45°C for 2-3 minutes and then to remove excess bath from the fabric by padding. The padded samples were dried 3 minutes at 80°C and cured 3 minutes at 110°C. After curing, the samples were neutralized by treatment in a bath containing 0.1% of sodium carbonate and 0.25% of Lux liquid detergent at 60°C for 15 minutes. The neutralized samples were rinsed in water at 45-50°C for 1 hour and finally in cold water for 1 hour. The rinse water was changed once at both temperatures. The samples were then dried at 100°C.

b. Other fluoroorganic pyridinium chlorides

The other fluoroorganic pyridinium chlorides were applied to the 3.3-oz/yd^2 cotton fabric in a manner similar to that used for application of FCAMPC. Some of the compounds contained a sticky material that did not dissolve in the padding bath. This material was separated from the pad bath, dried, and weighed, and the bath concentration corrected for the insoluble material. The conditions for application were 8% pad bath, 2-minute immersion time, 3-minute drying at 80°C, 3-minute curing at 110°C, washing and rinsing as described above, and final drying at 22°C and 65% RH.

6. N-Methylolperfluoropropylguanamine-THPC condensate

The solution containing perfluoropropylguanamine-THPC that was prepared as described in Section V-A-13 was diluted with 10 ml of water. The diluted solution was turbid, so 3 drops of Triton X-100 and 3 g of triethanolamine were added and the mixture was stirred for 2 hours in an attempt to obtain a stable solution. A sample (Sample 1) of bleached and desized cotton fabric (3.3 oz/yd^2) that weighed 0.8137 g (conditioned at 21°C and 65% RH) was padded with the solution. A second sample (Sample 2) of cotton fabric that weighed 0.8067 g (conditioned at 21°C and 65% RH) was padded with the solution after it had been stored for 48 hours at room temperature and the turbidity had disappeared. Both of the treated samples were dried 5 minutes at 150°C. The cured samples were washed 30 minutes in acetone, 1 hour in warm water (43-46°C), and 1 hour in running tap water. The samples were dried at 21°C and 65% RH.

Sample 1 weighed 1.139 g, indicating 40% solids add-on, and Sample 2 weighed 0.8067 g, indicating 37% solids add-on.

Samples 1 and 2 both had flame retardant properties as determined by the match test. A specimen of Sample 1 (151 mm long) burned 127 mm before the flame was extinguished. Sample 2 (145 mm long) burned completely but slowly. Neither sample was oil repellent, but both were water repellent. Both samples were penetrated instantly by bis(2-ethylhexyl) hydrogen phosphite. One minute after the drops of water were placed on the samples, the contact angles were 96° and 84° for Samples 1 and 2, respectively; 5 minutes after the drops were placed on the samples, the angles were 92° for Sample 1 and 72° for Sample 2.

7. *N*-Methylolperfluoroheptylguanamine-THPC condensate

A weighed sample of the desized and bleached cotton fabric, 3.3 oz/yd^2, was padded with the solution of the guanamine-THPC reaction product to apply 176% wet pickup. The sample was dried 5 minutes at 82°C and cured 8 minutes at 160°C, but the sample was discolored and had lost strength, indicating that the sample had been overcured. The treated sample was washed 30 minutes in ethanol, 1 hour in warm water (43-46°C), 1 hour in running tap water, and then it was dried at room temperature and weighed after conditioning. The solids add-on of this sample was 16.3%.

Another sample of the desized and bleached cotton fabric was padded with the treating bath to apply 110% wet pickup and then dried 4 minutes at 82°C and cured 3 minutes at 138°C. The sample was washed, dried, and weighed as described above. The solids add-on of this sample was 3.8%.

The properties of these treated samples were discussed in Section III-B-1-a.

8. Quarpel

The Quarpel bath was prepared to contain 8% Zelan AP and 14.3% FC-208 on a product basis. The Zelan AP was diluted with water at 60°C and mixed with an 0.8% aqueous sodium acetate solution following the manufacturer's prescribed procedure, except that a portion of the water was withheld for dilution of the FC-208. The FC-208 was diluted with warm water (38°C) and added to the solution of Zelan AP. Application to fabric samples was by padding with 100% wet pickup. The temperature of the bath was maintained at 45-50°C during padding. Treated materials were dried at 120°C for 5 minutes in a circulating air oven and then cured for 5 minutes in a circulating air oven at 175°C. The cured materials were neutralized 15 minutes at 60°C in a bath containing 0.1% of sodium carbonate bath and 0.25% of Lux liquid detergent. The neutralized materials were washed in water at 45-50°C for 1 hour, 1 hour in cold water, and then dried at 160°C for 3 minutes.

9. Zelan AP

Baths of Zelan AP paste were prepared by diluting the Zelan with water at 60°C and mixing the dilution with a solution containing one-tenth as much sodium acetate in accordance with the manufacturer's recommendations. Applications to fabrics were made by padding. The temperature of the baths was maintained at 45-50°C during padding and the wet pickup on cotton was 75%. The treated material was dried for 4 minutes at 120°C in a circulating air oven and then cured for 3 minutes at 175°C. After curing, samples were neutralized 30 minutes in a solution containing 0.1% of sodium carbonate and 0.25% of Lux liquid detergent at 50°C. The neutralized samples were rinsed in water at 45-50°C for 1 hour, and finally in cold running water for 1 hour. Finally, the samples were dried in an air circulating oven at 160°C for 3 minutes. Add-ons were determined by weighing.

10. FC-208

Samples of fabrics were padded with aqueous solutions of FC-208 with 100% pickup and then cured for 6 minutes at 150°C.

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APPENDIX A

EVALUATION PROCEDURES

1. Conditioning

All materials were conditioned at 21°C, 65% relative humidity for a minimum of 24 hours prior to evaluation of physical properties. The physical tests were made under these standard conditions of temperature and relative humidity.

2. Breaking strengths and elongation

The dry and wet breaking strengths and elongations at break were determined by ASTM Cut Strip Method D-39-49 with an IP-4 Scott Tester or a J-2 Scott Tester, depending on the strength of the material. Measurements were made in both the warp or machine direction and the filling or cross direction. Each value reported is the average of 5 individual tests.

3. Tearing strength

Tearing strength determinations were made with an Elmendorf Tearing Tester by ASTM Method D-1424-56T. Specimens from both the warp or machine direction and the filling or cross direction of the samples were tested, and each average tearing strength value reported is the average of 5 individual tests. The lowest and highest tearing strength values are reported as well as the average because of the wide variation in the individual tearing strengths of reinforced papers. Wet tearing strength was determined by the same procedure except that the specimens were immersed for 1 minute in water containing 0.05% Triton X-100 removed from the water and evaluated immediately.

4. Abrasion resistance

Abrasion resistance was determined by ASTM Method D-1175-55T with a Taber Abrader equipped with CS-10 calibrase wheels. The 1000-gram weights were used during all tests. The material was weighed, then abraded for 200 cycles or until a hole was worn through it. The abraded material from the specimens that were abraded for only 200 cycles was removed by a vacuum cleaner and the specimens reweighed and the results are reported as percent loss of weight. For all other specimens the results are expressed in cycles to rupture. For wet abrasion the test specimen was immersed in water containing 0.05% Triton X-100, and then abraded until a hole was worn through it.

5. Edge tear

Edge tear was determined by TAPPI Method T 470 M-S4 with a J-2 Scott Tester. The test specimens were 1-inch wide and 8-inches long with the long dimension parallel to the warp. Measurements were made only in the warp or machine direction. The results are expressed in pounds as measured on the 1 inch strip, and each value reported is the average of 3 individual tests. In retrospect, there is some doubt regarding whether this method is suitable for measuring the edge tear of the types of samples of interest in this project.

6. Bursting strength

Bursting strength was determined by ASTM Method D 231-46 using a Mullen Tester made by B. F. Perkins and Son, Inc. Results are expressed as psi and each value reported is the average of 3 individual tests.

7. Stiffness

Stiffness measurements were made with a Gurley Stiffness Tester with a loading weight of 25 grams attached to the pointer 1 inch below its center. The specimens were 0.5-inch wide and 1.5-inch long, with the long dimension in the warp or machine direction. Results are given in [illegible] and each value reported is the average of 3 individual tests.

8. Flexibility at low temperature

Impregnated paper samples were conditioned in a cold box for 30 minutes at a temperature of -55°C to -60°C and the flexibility was determined subjectively without removing the samples from the box.

9. Air permeability

Air permeability was determined with a Gurley Permeometer at a pressure drop across the material of 0.5 inch of water. ASTM Method D-735-43T was used. Results are expressed in $ft^3/min/ft^2$, and the value reported for each sample is the average obtained from 5 specimens.

10. Thickness

Thickness was determined with a Randall and Stickney gauge in accordance with ASTM Method D-39-49. Each value reported is the erage of 5 determinations.

11. Weight

The weight of the materials was determined according to ASTM Method D-39-49. Results are expressed as oz/yd^2 and are the averages of 3 determinations.

12. Wrinkle recovery

Wrinkle recovery tests were made on paper handsheets with the Monsanto Wrinkle Recovery Tester. The values reported are the averages of 3 measurements.

13. Peel strength

Reinforced papers consist of scrim or strands of yarn sandwiched between two layers of fibers. Peel strength, as used in this report, is the maximum pull required to separate both layers of paper simultaneously from the reinforcing strands. A specimen of paper 1-inch wide and 4-inch long was used for the test. The upper and lower layers of fibers were separated by hand from the reinforcing yarns for a distance of 3 inches. One layer of the paper was clamped in one of the jaws of an IP-4 machine; the other layer was clamped in the other jaw leaving the yarns free. The jaws were 3-inches apart. A 1-inch x 1-inch area of the specimen remained in tack for testing. The maximum value recorded by the machine when the layers in this area were separated was taken as the peel strength. Each value reported is the average of 3 individual tests.

14. Water-vapor transmission rate

Water-vapor transmission rates were determined with Payne permeability cups by ASTM Method E-96-537. The cups are designed so that an area of the specimen 10 cm is tested. The tests were made at 22°C with 100% relative humidity on one side of the material being tested and 50% relative humidity on the other side. Each value reported is the average of 2 individual tests.

15. Water repellency

ASTM Method D 583-54 was used for determining the resistance of the materials to water spray. Each value reported is the average of 3 individual measurements.

16. Flame resistance

Flame-resistant properties were determined by the Vertical Buns test, ASTM Method D 626-55T. The Vertical Bunsen test consists essen of applying a 1.5-inch luminous flame to the lower end of a 12-inch specim supported in a vertical position and clamped in a holder so that a 2-inch is exposed. The specimen is held 0.25-inches above the top of the gas bu and the flame is applied for 12 seconds.

Observation of after-flame, after-glow, and char length are made. After-flame is measured by the time in seconds that the specimen continues to flame after removal of the flame. When flaming ceases, glowing is allowed to continue until it stops naturally. The time in seconds that the sample glows or smolders after removal of the flame is recorded as the after-glow. Char-length is the distance from the lower end of the specimen that was exposed to the flame, to the end of a tear produced by raising one lower corner of the specimen until it lifts a 2 ounce weight attached to the other lower corner. Specimens are considered flame-resistant if the after-flame does not exceed 2 seconds and if the char-length does not exceed 4 inches. There is no precise limit for after-glow but it should be of short duration.

17. Tackiness at elevated temperature

Impregnated paper samples were heated for 30 minutes at 45°C in a circulating air oven. The tackiness of the samples was determined subjectively at the elevated temperature and compared to control samples that had not been heated.

18. Puncture strength

A 3 x 3-inch specimen of the material is placed across the end of an aluminum tube 1.5-inch high and 1.375-inch inside diameter, and clamped around the sides of the tube. The tube is placed on the stationary platen of the compression cage of the Instron Tensile Tester, Model TM, with the specimen at the top of the tube. A 0.16 inch diameter rod rounded at the bottom end is fastened to the moveable platen. The puncture rod is lowered at the rate of 1 inch per minute until it punctures the specimen, and the force required is read from the chart. Measurements are made on 5 specimens and the values are averaged. The results are expressed in pounds.

19. Water resistance of cloth

Details of this method are given in Dynamic Absorption Method 5500, Federal Specification Textile Test Methods, CC-T-19b, May 15, 1951.

In this method, samples are tumbled in a drum containing water. After a given length of time, the samples are removed from the drum and passed through squeeze rolls. The percentage increase in weight is reported.

20. Water leaching

Details of this method are given in AATCC Tentative Test Method 30-52, part C-1.

In this method, samples are leached in running water at 30°C for 24 hours.

21. Seam separation strength

Seam separation strength, as the term is used in this report, is th maximum pull required to separate the two layers of an overlap seam. Th seams were made with 1 inch overlap and 1 x 6 inch specimens were cut across the seam with the seam at approximately the center of the strip. The bonded area of each specimen was therefore, 1 x 1 inch. The specim were clamped in a Scott IP-4 tensile test machine with the jaws 3 inches apart and with the seam centered between the jaws. The maximum value recorded by the machine when the seam separated was taken as the seam separation strength. Each value reported is the average of 5 determinat and the results are expressed in lb/in. of width.

22. Seal strength

Seal strength, as used here, is the maximum pull required to separate plastic film from the paper material to which the plastic has been heat sealed. Specimens 1 x 4 inches were cut and clamped lengthwise in an IP-4 machine with the jaws 1 inch apart. The maximum pull required to separate the film from the paper was taken as the seal streng Each value reported is the average of 5 determinations and are expresse in lb/in. of width.

23. Contact angles

TAPPI Method T-458-M-59 was followed for determining conta angles. The apparatus that was used for the determinations consists of the following parts:

(a) A. O. Spencer adjustable lamp for illuminating the test specimen.

(b) A. O. Spencer Model P42AC microscope mounted horizontally. The microscope is equipped with a 2 2x objective and a 10x eyepiece.

(c) E. Lietz Micam Camera that has a removable ground-glass plate for viewing and focusing. The camera makes $3\frac{1}{4}$ x $4\frac{1}{4}$-inch pictures.

(d) Micro-syringe with a 20-gauge needle.

The samples and test liquid were conditioned at 21°C and 65% relative humidity for 24 hours, and the contact angles were determined at the same conditions. The edge of one end of a test specimen of garment material was glued to a microscopic slide; then, while the specimen was pulled to remove wrinkles, the other edges were glued. The mounted test specimen was placed on the stage of the microscope, and a 0.07 ml drop of liquid from a hypodermic needle was deposited on the surface of the specimen. The tip of the needle was approximately 2.5 mm from the surface of the specimen. The profile of the drop was projected on the ground-glass plate of the camera and brought into focus. The ground-glass plate was then replaced with photographic paper, and one minute after the drop was deposited, a picture was taken. A line was drawn on the picture to represent the base of the drop, then tangents to the drop were drawn at the points of solid-liquid-air interfaces. The contact angles were measured with a protractor, and the maximum angle was recorded as the advancing angle.

If a material has good repellency for the liquid, the rate of penetration can be estimated by determining the maximum contact angle again after the drop has been on the surface of the specimen for 5 minutes. The rate of penetration, expressed as the rate at which the angle of wetting changes in degrees/minute, is equal to the contact angle after 1 minute minus the contact angle after 5 minutes divided by 4.

24. Methods for screening garment materials for resistance to liquid CW simulants and agents

The following observations were made in screening garment materials for resistance to penetration by liquid CW simulants and agents: (1) observation of the behavior of droplets of the liquid applied to the material, (2) determination of the time required for the liquid to be absorbed by the material, and (3) determination of the time required for the liquid to penetrate the thickness of the material. The penetration time was determined under two conditions: with no pressure and with pressure on the liquid.

Bis(2-ethylhexyl)hydrogen phosphite was used as a simulant for the agents. GA, GB, HD, and VX are the live agents that were used. The simulant and agents were colored with an oil-soluble dye to aid detection.

The general procedure consists of placing small droplets of the liquid on one surface of the material, held under constant tension and noting the time required for the first appearance of any liquid on the opposite side; the time required for the liquid to disappear from the surface by absorption or by evaporation; and the shape and maximum length of the wetted area.

In making these determinations, a 235-g weight is attached to each end of a 2 x 4-inch piece of the garment fabric and the assembly is hung over a horizontal glass tube, 40 mm in diameter, with a piece of absor filter paper between the fabric and the glass. A 7 to 8-mg drop of the colored simulator agent, is placed on the fabric by means of a microsyr held with the tip approximately 3 mm from the surface. A prism is m under the tube to facilitate observation of penetration.

The several effects that may be observed when a drop of a liquid is applied to a specimen are:

(a) The drop does not wet the material initially, but remains pearled on the surface for various lengths of time before evaporating or wetting and sinking into the specimen.

(b) The drop wets and sinks into the body of the material but does not wick out rapidly.

(c) The drop enters the material immediately and wicks out rapidly in an elongated pattern.

(d) The drop enters the material immediately and wicks out rapidly and uniformly in all directions to form a circular pattern.

When actual CW agents were used, measurements were made in the apparatus shown in Figure 1. Essentially, this apparatus is a small hood containing a glass mandrel, a chrome-plated bar with an attachment for lding a microsyringe and for allowing the syringe to be moved over the length of the mandrel, a microsyringe, and a prism. The samples and the syringe may be reached through the two holes in the front panel of the apparatus. A blower and a compartment filled with activated charcoal are on the back of the apparatus. The apparatus is housed in a hood equipped with a charcoal filter in the stack; the hood has an air velocity greater than 100 cfm.

The method described above is modified slightly for determining the penetration time of liquids under pressure. For this purpose, the specimen is placed on a horizontal plate of glass, with a piece of filter paper between it and the glass, and unless otherwise noted a 7 to 8-mg drop of liquid is placed on the specimen as before. Fifteen seconds later, a metal weight that exerts a pressure of 1 psi is placed centrally on the drop of liquid. The weight is kept in place for one minute and penetration is observed visually through a prism located beneath the sample. The time required for penetration is reported in seconds, starting at the instant the weight is placed on the specimen.

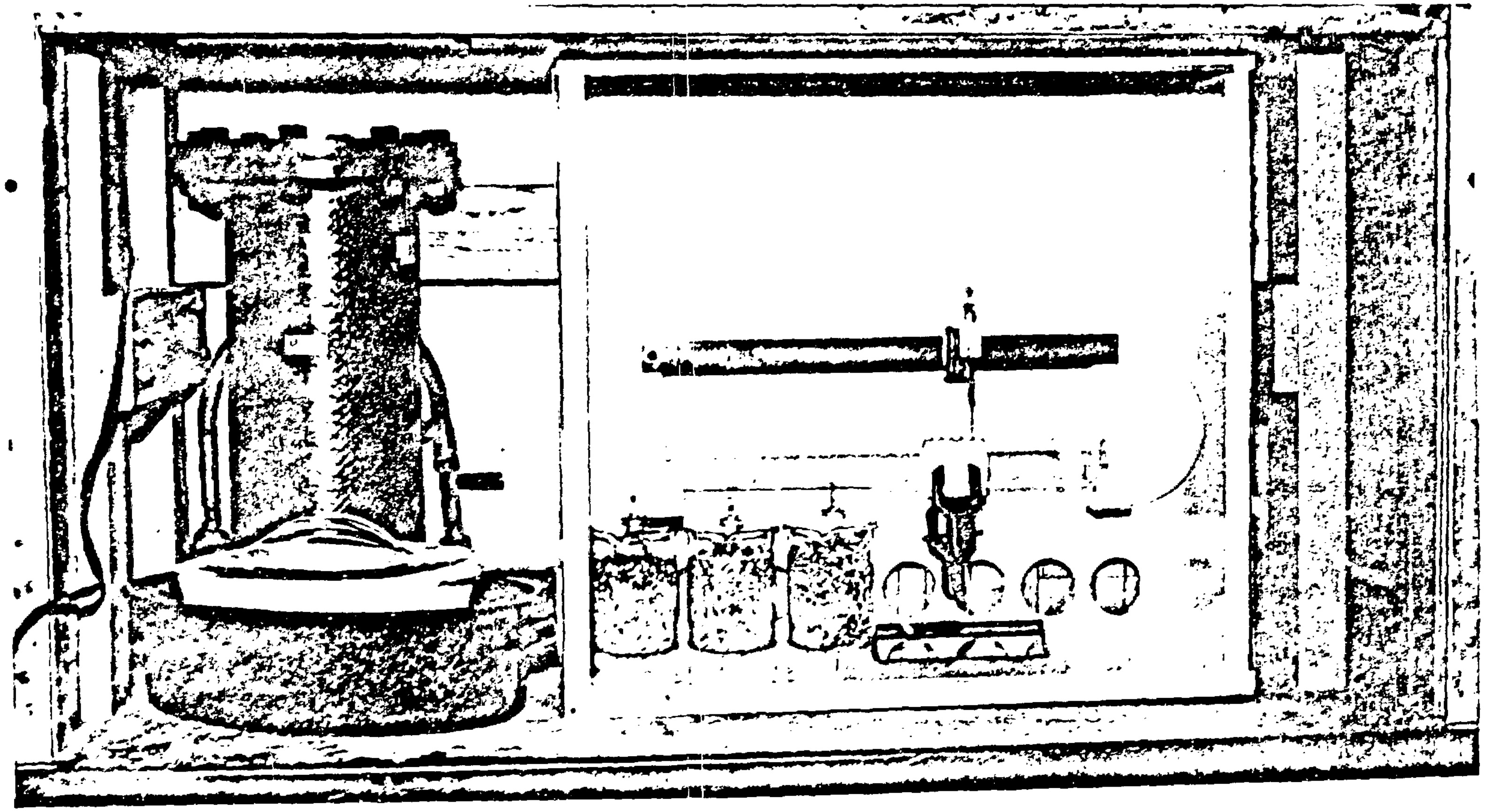

Figure A-1. Apparatus Used with Active CW Agents

25. Description of apparatus and procedure for determination of aerosol filtration efficiency

A di-n-octyl phthalate (DOP) aerosol in air was produced by a generator similar to the one described by Sinclair and Le Mer.[1] This apparatus consists of two 3-liter flasks, one called the boiler, the other called the reheater. The boiler, which contains about 1.5 liters of DOP, is equipped with 2 tubes, through which dry air is admitted, and a corona-discharge tube. Each air-inlet tube contains a needle value and a roto-meter-type flow meter. One air stream is bubbled into the liquid and the other one passes across an A.C. high voltage spark gap and then into the vapor-containing portion of the flask. A mist of DOP, ions produced from the corona discharge in air at the spark gap, and dry air is led from the boiler into the reheater In the reheater, the DOP evaporates and subsequently condenses with the ions in the air stream, which serve as nuclei for the minute droplet formation.

The following conditions were experimentally determined for producing an aerosol containing 4.6 mg of DOP per liter at a rate of 4 liters per minute; boiler at 190°C, reheater at 240°C, a rate of air flow into the DOP of 3.3 liters per minute, and a rate of air flow through the 20,000 volt spark gap of 0.7 liter per minute.

The particle size of the aerosol droplets were determined by measuring the rate of settling of the particles. A 1-liter graduated cylinder was filled with the aerosol by displacing the air that was in the graduate. After filling, the aerosol delivery tube was removed from the graduate and the upper, open end of the graduated cylinder was covered with a watch-glass. The movement of the settling aerosol was measured with a meter stick. The average particle size of the aerosol was 2.4μ in diameter, as determined from the rate of settling measurements. During settling, the aerosol had a well defined front. Sinclair[2] has interpreted such a boundary condition to be indicative of a narrow particle-size distribution.

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1. D. Sinclair and V. K. La Mer, Chem. Reviews 44, 254 (1949).

2. D. Sinclair in "Air Pollution," L. McCabe, Ed., McGraw-Hill Book Company, Inc., New York, 1952, pp. 169-171.

The aerosol stream from the generator was split. Some of it was discharged to the fume hood, and the rest was diluted with dry air so that the concentration was approximately 1 mg of DOP per liter and the flow rate was 5 liters per minute. This diluted stream was then led to a sample holder through a pressure regulator, consisting of a "T" in the aerosol line with a drop-tube submerged in water. A water depth of about 6 inches, corresponding to approximately 0.25 psi, gave the maximum pressure at which the aerosol generator and dilution system would operate. The sample to be evaluated was clamped between a pair of steel, bell-shaped cups so that a circular portion of the sample, approximately 5 cm in diameter, was exposed to the aerosol stream for 5 minutes. Static pressure lines were connected to the apparatus so that the pressure drop across the sample could be measured. These pressure drops were between 0.01 and 0.2 inch of water, depending on the porosity of the sample. With exceedingly porous samples, two layers of the filter media were used. This maximum pressure and the porosity of the sample then determined the upper limit of the volume of aerosol that would pass into the sample holder.

Downstream from the sample holder was a flange-type union that accomodated a 3-cm diameter circle of glass filter paper (Mine Safety Appliances Company, Type 1106-BH Filter Paper). This filter paper trapped the aerosol and served as a measuring device. After use, the paper was extracted with ethanol, and the quantity of DOP in the resultant solution was determined spectrophotometrically. Immediately after a given filter medium was exposed to the aerosol stream, a blank determination was made with the apparatus under identical conditions, except that no sample was present. From the analytical data it was possible to calculate the filtering efficiency of the sample, or that portion of the aerosol retained by the filter medium.

An electronic particle size counter was assembled and used in some evaluations. The counter indicated the number of particles present in a unit volume, and also measured the particle size distribution.

26. Oil repellency

The 3M test was used for evaluating the oil repellency of samples. This test is based on the difference in the penetrating or wetting properties of mineral oil and *n*-heptane. The two liquids are miscible in all proportions and exhibit greater wetting power as the amount of *n*-heptane in the mixture is increased.

The oil repellency rating assigned to each of the eleven test oils that are used are given in Table A-1. To measure the oil repellency of a treated fabric by the 3M method, drops of the tests oils are gently placed on the fabric and allowed to stand undisturbed for 3 minutes. The number corresponding to the mixture containing the highest percentage of heptane which does not penetrate or wet the fabric is considered the oil repellency rating of the test material.

The oil repellency values determined by this method have been found to correlate with actual resistance of materials to oily stains. Fabrics with an oil repellency rating of 50-70 have only fair resistance to oil staining; fabrics with an oil repellency rating of 80-90 have good resistance to oil staining; and fabrics with oil repellency ratings of 100 or greater have excellent resistance to oil staining.

27. Laundering procedure

For evaluations of durability of the finishes to laundering, samples were washed in a Maytag automatic washer, Model 132. The washing cycle consisted of washing 14 minutes at 77°C with 0.25 cup of Tide, extracting 2 minutes, wet spinning 0.5 minute, rinsing 2 minutes, and extracting 4.5 minutes. The samples were then dried in a Westinghouse clothes dryer (Model D-112), rinsed 10 times in distilled water at 49°C, and air dried.

Table A-1. Compositions of Liquid Mixtures for the 3M Oil Repellency Test[a]

Oil repellency rating	Percent mineral oil[b]	Percent n-heptane
150	0	100
140	10	90
130	20	80
120	30	70
110	40	60
100	50	50
90	60	40
80	70	30
70	80	20
60	90	10
50	100	0
0	(immediate penetration by mineral oil)	

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[a] E. J. Grayjeck and W. H. Peterson, Textile Research J. 32, 320-331 (1961).

[b] "Nujol", percent by volume.

28. Procedure for determination of penetration of vapor from liquid CW agents

Pieces of flank pigskin, 1.5 x 2.5 inches, with as much of the fat removed as possible but with the dermis intact were attached to the underside of specimens to be evaluated with the dermis against the specimen. These assemblies were placed on aluminum plates with the specimens on top.

Evaluations with VX and HD were conducted at 35°C, but tests with GB were conducted at room temperature. The agents labelled with P^{32} (VX and GB) and S^{35} (HD) were applied as single 4 mg free-falling drops from a 27 gauge needle held close to the specimen. Drops of VX and HD were allowed to remain on the surface of the fabric for 24 hours, but the GB was left on the fabric for only 6 hours.

At the end of an exposure period, the piece of pigskin was put immediately into a beaker containing 20 ml of concentrated nitric acid and digested at 60°C. The residual fat, which separated as a liquid layer, was taken up in benzene, and the benzene and acid layers were separated. The two layers were diluted to 100 ml with benzene and water, respectively. Two 1.0-ml aliquots of each diluted layer were assayed in a liquid scintillation spectrometer, Packard Model 314 EXTRI-CARB.

With each group of pigskin pieces processed, controls, to which a known amount of the agent had been applied were also processed. For a control, a 4 mg drop of an agent was placed on a piece of the pigskin, and the pigskin was immediately digested and the fat was processed as described above. The total activity observed in the benzene and nitric acid layers from an unknown relative to the activity observed for the control provided a measure of the amount of penetration of an agent. The results are reported as μg of agent penetrating a system and also as the percentage by weight of a 4-mg drop. Determinations were made on two specimens of each experimental material, and the results are the averages of the two values.

29. Accelerated aging

Samples were stored at 80°C for 16 hours in an individual container containing a beaker of water to provide high humidity.

30. Match test

This method consists of suspending a strip of fabric $\frac{1}{4}$-inch wide by 8-inch long in a draft-free area and igniting the sample at the lower end with an ordinary match. The height of burning is noted visually and the results are expressed by four general classifications of flame resistance: "excellent" if the fabric does not burn after removal of the igniting flame, "good" if the burning is self-extinguished in the lower 3 or 4 inches of the strip, "fair" when the burning extends approximately 5 inches up the strip, and "fail" when the strip burns completely.

APPENDIX B

MATERIALS

ADHESIVES

Trade name	Description	Solids, %	Source
Adhesive KS-2	85% Plastisol (Geon 135 in dioctyl phthalate) and 15% Skellysol (mineral spirits)	-	Kimberly-Stevens Corporation
A[illegible]CO S-377	Vinyl chloride-acetate copolymer	paste	The Borden Company, Chemical Division
Bostick 4034	Synthetic rubber resin	35	B&B Chemical Company
CV-794	Vinyl emulsion type adhesive	49	The Borden Company, Chemical Division
CVV	[a]		Herculite Protective Fabrics
EC-784	Oil soluble elastomer	60	Minnesota Mining & Manufacturing Company
EC-1729	Synthetic rubber based	-	Minnesota Mining & Manufacturing Company
EZ-1904	Vinyl chloride	38	Permacel Adhesives
Formica Contact Cement	-	27	American Cyanamid Company
Kymene	Unknown	-	Hercules Powder Company
N-159	Neoprene in solvent	23	Union Bay State Chemical Company
Polyester 46971	Polyester in 1, 1, 2-trichloroethane	15	E. I. du Pont de Nemours and Company, In
PR-153	Resinous glue	100	The Borden Company, Chemical Division
Rhoplex E-32	Self-crosslinking acrylic emulsion	46	Rohm and Haas Company
Resiweld	Epoxy-based adhesive for nylon	-	The N. B. Fuller Company
Splic-It	Neutral color cement	93	The Borden Company, Chemical Division
SWB-952 (A&B)	Neoprene in solvents	24	Interchemical Corporation, Angiers Adhe[illegible] Department
Ubabond H-511	Acrylonitrile-rubber	28	UBS Chemical Company
U. S. Royal Industrial Adhesive M-6256	Thermoplastic	90	U. S. Rubber Company
Vistanex L-120	Isobutylene polymer	100	Enjay Company, Inc.
Vistanex M, Type MH	Isobutylene polymer	100	Enjay Company, Inc.
Vultex 1-S-1009	Compounded latex	57	General Latex & Chemical Corporation
Vultex 1-S-1052	Compounded latex	64	General Latex & Chemical Corporation
X-210-B	Compounded latex	60	Adhesive Products Corporation (Rubber Adhesives)

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[a] Recently developed; no specifications available.

CHEMICALS

Acetic acid	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Acetone	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Acetylene	Post Welding Company
Aluminum sulfate	Reagent grade, from Baker and Adamson
Ammonium bromide	From Mallinckrodt Chemical Works
Ammonium hydroxide	Reagent grade (28%), from General Chemical Division, Allied Chemical Corporation
Ammonium sulfamate	Practical grade, from Eastman Organic Chemicals Company
Antifoam A	A silicone compound from Dow Corning Corporation
Antimony trichloride	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Antimony trioxide	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Benzene	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Bis(2-ethylhexyl)hydrogen phosphite	From Virginia-Carolina Chemical Corporation
Borax	Technical grade, from United States Borax and Chemical Corporation
Boric acid	Reagent grade, from J. T. Baker Chemicals Division, Vick Chemical Corporation
Bromoform	Reagent grade, from General Chemical Division, Allied Chemical Corporation
2-Butanone	Reagent grade, from Eastman Organic Chemicals
Butyl cellosolve	Technical grade, from Union Carbide Chemical Company
Cab-O-Sil	Ultrafine pyrogenic silica from Cabot Corporation
Carbon tetrachloride	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Catalyst A	An inorganic acid-forming salt from Rohm and Haas Company
Catalyst CE	Catalyst, from Mobay Chemical Company
Catalyst H-7	35% solution of zinc complex, from Rohm and Haas Company
CC-3	Chloramide from Army Chemical Center
Cellosize WP-09	Hydroxyethylcellulose, from Union Carbide Chemical Company
Chlorowax 40	Chlorinated alkane, from Diamond Alkali Company
Cyanuric chloride	Obtained from American Cyanamid Company
Darco KB	Activated carbon, from Atlas Powder Company
Darco S-51	Activated carbon, from Atlas Powder Company
Daxad 11	Surfactant, from Dewey and Almay Chemical Company
Diammonium phosphate	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Dibutylphthalate	Obtained from Fisher Scientific Company

CHEMICALS (continued)

Dicyandiamide	Obtained from American Cyanamid Company
Dimethyl hydrogen phosphite	Obtained from Virginia-Carolina Chemical Corporation
Di-octylphthalate	Reagent grade from Eastman Organic Chemicals
Ethanol	From U. S. Industrial Chemical Company
Ether	Reagent grade, from General Chemical Division, Allied Chemical Corporation
C_8 and C_{11} Fluoroalcohols	Technical grades, from E. I. du Pont de Nemours and Company, Inc.
Formaldehyde	Reagent grade (37%), from General Chemical Division, Allied Chemical Corporation
P^{32} labelled GB	From Canadian Defense Research Laboratories; activity 50 mc/ml
Heptafluorobutyric acid	Obtained from Peninsular ChemResearch, Inc.
Heptafluorobutyronitrile	Obtained from Peninsular ChemResearch, Inc.
S^{35} labelled HD	From Nuclear-Chicago Corporation; activity 6 mc/0.028 ml. Diluted with non-radioactive material to give 6 mc/ml
Hydroquinone	Reagent, from Distillation Products Industries Division of Eastman Kodak Company
Hydrochloric acid (gas)	From the Matheson Company, Inc.
Hylene MP	Adduct of Bisphenol-A and methylene bis(4-phenyl isocyanate), from E. I. du Pont de Nemours and Company, Inc.
Hylene TM	Toluene diisocyanate, from E. I. du Pont de Nemours and Company, Inc.
Igepal CO-850	Surfactant, from Antara Chemical Company
Mercuric oxide	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Methyl alcohol	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Mondur CB-75	Curing agent, from Mobay Chemical Company
Morpholine	Reagent grade, from E. H. Sargent and Company
Niax PPG 2025	Polyether, from Union Carbide Chemical Corporation
n-Octyl alcohol	Reagent grade, from Eastman Organic Chemicals
Oleic acid	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Orthophosphoric acid	Reagent grade (75%), from General Chemical Division, Allied Chemical Corporation
Paraformaldehyde	From Eastman Organic Chemicals
Perclene	Tetrachloroethylene, from E. I. du Pont de Nemours and Company, Inc.
Perfluorobutyramide Perfluoropropionamide Perfluorooctanoic acid	Obtained from Peninsular ChemResearch, Inc.
Potassium hydroxide	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Potassium permanganate	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Phosphorous pentoxide	Reagent grade, from General Chemical Division, Allied Chemical Corporation

CHEMICALS (continued)

Pyridine	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Release Gen Type S-1	Silicone mold release agent from Dow Corning Corporation
Resloom HP	Trimethylolmelamine (powder), from Monsanto Chemical Company
Santomerse SX	Sodium alkylaryl-sulfonate solution, from Monsanto Chemical Company
Santomerse 85	Sodium-alkylaryl-sulfonate solution, from Monsanto Chemical Company
L-520 Silicone Oil	Surfactant, from Union Carbide Chemical Corporation
S-330	Chloroamide, from Army Chemical Center
Skellysolve "B"	Essentially n-hexane, from Skelly Oil Company
Sodium (metallic)	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Sodium acetate	Anhydrous reagent grade, from General Chemical Division, Allied Chemical Corporation
Sodium bicarbonate	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Sodium carbonate	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Sodium hydroxide	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Sulfamic acid	Practical grade (100%), from General Chemical Division, Allied Chemical Corporation
Sulfuric acid	Reagent grade (95-96%), from General Chemical Division, Allied Chemical Corporation
Sulfur dioxide	From The Matheson Company, Inc.
"Tergitol" penetrant 08	Surfactant, from Carbide and Carbon Chemicals
Thionyl chloride	Reagent grade, from Eastman Organic Chemicals
Thiourea	Reagent grade, from Eastman Organic Chemicals
D-33 Tin dilaurate	Catalyst, from Union Carbide Chemicals Corporation
Toluene	Reagent grade, from General Chemicals Division, Allied Chemical Corporation
p-Toluene sulfonic acid	Reagent grade, from Eastman Organic Chemicals
Triallyl phosphate	Technical grade, from Borden Chemical Company
Triethanolamine	Reagent grade, from Eastman Organic Chemicals
Triethylene diamine	Catalyst, from Union Carbide Chemical Corporation
Triton X-100	Iso-octyl phenoxy polyethoxy ethanol, nonionic surfactant (100% active), from Rohm and Haas Company
Urea	Reagent grade, from General Chemical Division, Allied Chemical Corporation
P^{32} labelled VX	From Canadian Research Defense Laboratories; activity 50 mc/ml
Xylene	Reagent grade, from General Chemical Division, Allied Chemical Corporation
Zinc fluoroborate	40% solution, from Harshaw Chemical Company
Zinc nitrate $\cdot$ $6H_2O$	Reagent grade,from General Chemical Division, Allied Chemical Corporation

COMMERCIAL SCRIMS

Dixienet 551-40047	A 6-mesh cotton scrim weighing 2.2 oz/yd^2, from Swift Manufacturing Company
Scrim Style BR-36	A 4-mesh rayon scrim weighing 1.0 oz/yd^2, from Wellington Sears
Scrim Style 150	A leno weave nylon scrim, from Southern Press and Filter Media Company

CW AGENT GELLING MATERIALS

CMC Type 70D High	A high molecular weight carboxymethylcellulose, supplied by Hercules Powder Company
Methocel 1,500 cps	A methylcellulose of high molecular weight, supplied by the Dow Chemical Company
Polectron 130	A copolymer of vinylpyrrolidone and ethyl acrylate, supplied by Antara Chemicals Division, of General Aniline and Film Corporation
Polectron 430 and 450	A copolymer of vinylpyrrolidone and styrene. The 450 type has a higher vinylpyrrolidone to styrene ratio than 430. Made by Antara Chemicals Division of General Aniline and Film Corporation
PVP, Types K-30, K-60, K-90	Technical grade of poly(vinylpyrrolidone). The three types differ in the size of the polymer and are listed above in order of increasing molecular weight. Supplied by Antara Chemicals Division of General Aniline and Film Corporation
PVP/VA W-464	A copolymer of vinylpyrrolidone and vinyl acetate, made by Antara Chemicals Division of General Aniline and Film Corporation

FIBERS

Cellulose acetate	2.5-denier, 0.25-inch staple, Type 4W dull, made by Celanese Fibers Company
Cellulose acetate	3.0-denier, 2-inch staple cellulose acetate, dull, made by Celanese Fibers Company
Cotton linters	First cut cotton linters Type 1-P-500f were supplied by the Buckeye Cellulose Corporation
Dacron	1.5-denier, 0.25-inch staple, Type 54 Dacron, made by E. I. du Pont de Nemours and Company, Inc.
Dacron D-90	2.5-denier, 0.25-inch staple Dacron, made by E. I. du Pont de Nemours and Company, Inc.
Fibrids 101	Fibrous synthetic polymer binder made by E. I. du Pont de Nemours and Company, Inc. The morphology is somewhat similar to that of beaten wood pulp. Fibrid binders are supplied as a damp cake of 20% solids.
Fibrid 201	A fibrous synthetic polymer binder made by E. I. du Pont de Nemours and Company, Inc. The morphology is somewhat similar to that of beaten pulp. Fibrid binders are supplied as a damp cake of 20% solids.
Harmac kraft	Semi-bleached kraft pulp, obtained from Kimberly-Stevens Corporation
Nylon	1.5-denier, 0.25-inch staple, Type 221 nylon, made by E. I. du Pont de Nemours and Company, Inc.
Nylon	1.5-denier, 0.25-inch nylon staple, obtained from Kimberly-Stevens Corporation
Nylon	3.0-denier, 0.37-inch nylon staple, obtained from Kimberly-Stevens Corporation
Nylon	1.5-denier, 1.5-inch staple nylon, Type 203, made by E. I. du Pont de Nemours and Company, Inc.
Polypropylene	2-denier, 0.25-inch staple, supplied by Claremont Flock Company
Poly(vinyl alcohol)	1.0-denier, 0.37-inch staple, Vinal fibers made by Air Reduction Chemical Company
Rayon	1.5-denier, 0.25-inch staple, Type XL rayon made by American Viscose Corporation
RD 101	1.5-denier, 0.25-inch staple, Type RD 101 rayon fiber. RD 101 is a multi-cell rayon fiber made by American Viscose Corporation. It is supplied as a matty crumbly mass of dry fiber which wets out quickly, swells and separates when placed in water.
Wood pulp	Semi-bleached (approximately 80 brightness) kraft pulp obtained from International Paper Company was used. The pulp is kept in the form of dried sheets, resembling heavy paper board; the sheets are disintegrated in water as needed for the experiments.

FILMS AND FOAMS

Films and foams	Source	Description	Weight, oz/yd^2
Disposable Safety Suit	Safety First Supply Company	poly(vinyl chloride) film	3.0
Herculite Micro-Vent	Herculite Protective Fabrics, Inc.	a microporous film containing a scrim	4.0
Mylar	E. I. du Pont de Nemours and Company, Inc.	1-mil and 5-mil films	-
Nylon	Polymer Corporation of Pennsylvania	3-mil and 5-mil films	-
Polyethylene	Visking Company	5-mil and 10-mil films	-
Polyethylene	E. I. du Pont de Nemours and Company, Inc.	3-mil, low density	-
Polyethylene boots	[a]		-
Polyurethane foam/nylon fabric laminate	Duplan of Canada	3/32-inch polyester	4.7
Polyurethane	Duplan of Canada	block	-
Polyurethane foam/nylon fabric laminate	Project Officer	polyester foam treated with carbon/ Hycar 2671	-
Polyurethane foam	Reeves Brothers, Inc.	3/32-inch polyester	-
Reynolon 4-6	Reynolds Metals Company	poly(vinyl alcohol) film	4.0
Scottfoam	Scott Paper Company	polyurethane	1.5

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[a] Boots obtained from Quartermaster Research and Engineering Command and given to them by Naval Radiological Defense Laboratory.

FIRE RETARDANTS

Abopan	A complex sodium borophosphate from Glyco Chemicals Division, Charles L. Huisking and Company, Inc.
Apex Flameproof 290-B	Water-soluble fire retardant (25% solids) made by Apex Chemical Company, Inc.
Arko Fire Retardant 98-B	Water-soluble flame retardant (100% solids) made by Arkansas Company, Inc.
Fi-Retard NBX	Water-soluble flame retardant from the Arkansas Company, Inc.
Fire Retardant L-2	Water-soluble flame retardant from Burkart-Schier Chemical Company
Fire Retardant RC	General purpose flame retardant (100% solids) from Burkhart-Schier Chemical Company
Fire Retardant X-12	An ammonium sulfamate type, non-durable flame retardant from E. I. du Pont de Nemours and Company, Inc.
Pyroset DO	An organic phosphate compound from American Cyanamid Company
Pyroset Fire Retardant N-2	A stable urea formaldehyde syrup (85% solids) from American Cyanamid Company
Pyroset N-10	A urea-formaldehyde copolymer condensate (80% solids) from American Cyanamic Company
Tris-1-aziridinyl phosphine oxide (APO)	A durable flame retardant (85% solids) from Chemir Corporation
Tris-1-aziridinyl phosphine sulfide (APS)	A durable flame retardant (crystalline, 95% minim purity) from Chemirad Corporation
Tris(2-methyl-1-aziridinyl)phosphonium sulfide (MAPS)	A durable flame retardant (85% solution in ethanol) from Interchemical Corporation
Tetrakis(hydroxymethyl)-phosphonium chloride (THPC)	A durable flame retardant (95% purity) from Oldb ElectroChemical Company

LATEXES AND BINDERS

Trade name	Description	Manufacturer	Solids, %
Aerotex Resin M-3	melamine-formaldehyde condensate	American Cyanamid Company	-
Baymal	colloidal alumina consisting of minute fibrils of boehmite (ALOOH) alumina	E. I. du Pont de Nemours and Company, Inc.	100
Chemigum 245 CHS	dispersion of 67:33 butadiene-acrylonitrile copolymer	Goodyear Tire and Rubber Company	42.5
Dow Latex 512K	dispersion of a 40:60 butadiene-styrene copolymer	Dow Chemical Company	48.0
Elastothane	polyurethane elastomer	Thiokol Chemical Company	-
Gen-Tac	dispersion of vinyl pyridine latex	The General Tire and Rubber Company	40.8
Geon 351	poly(vinyl chloride) latex	B. F. Goodrich Chemical Company	55-57.5
Geon 427	copolymer of vinyl chloride and vinyl acetate	B. F. Goodrich Chemical Company	100
Geon 576	dispersion of poly(vinyl chloride) and dioctyl phthalate plasticizer	B. F. Goodrich Chemical Company	55-57.5
Geon 577	similar to Geon 576, but with a non-flammable plasticizer, presumably an organic phosphate	B. F. Goodrich Chemical Company	55
Hycar 1561	aqueous dispersion of a butadiene-acrylonitrile copolymer	B. F. Goodrich Chemical Company	40
Hycar 1552	aqueous dispersion of a butadiene-acrylonitrile copolymer	B. F. Goodrich Chemical Company	50
Hycar 1572	aqueous dispersion of a carboxy modified butadiene-acrylonitrile copolymer	B. F. Goodrich Chemical Company	50
Hycar 2600 X-30	aqueous dispersion acrylic polymer, non-ionic containing carboxylic groups	B. F. Goodrich Chemical Company	50
Hycar 2600-92	aqueous dispersion of an acrylic polymer	B. F. Goodrich Chemical Company	50
Hycar 2671	poly(acrylic ester)	B. F. Goodrich Chemical Company	50
Hycar 2600 X 83	aqueous dispersion of an acrylic polymer	B. F. Goodrich Chemical Company	51

LATEXES AND BINDERS (continued)

Trade name	Description	Manufacturer	Solids %
Hycar 4501	aqueous dispersion of an acrylic ester resin, anionic	B. F. Goodrich Chemical Company	50.4
Lexan 125	polycarbonate resin	Mobay Chemical Company	100
Multranil 176	polyurethane resin	Mobay Chemical Company	100
Neoprene 842A	aqueous dispersion of neoprene	E. I. du Pont de Nemours and Company, Inc.	50
Natural Rubber Latex	latex	Heveatex Corporation	40
Orinite 24	polybutene	California Chemical Company	-
Parlon S-20	chlorinated rubber	Hercules Powder Company	100
Piccolyte S-115-L	terpene resin	Pennsylvania Industrial Chemical Corporation	100
Rhonite 401	thermosetting resin used for crosslinking	Rohm and Haas Company	55[a]
Rhoplex AC-33	aqueous dispersion of an acrylic polymer	Rohm and Haas Company	46
Rhoplex B-15	aqueous dispersion of an acrylic polymer	Rohm and Haas Company	46
Rhoplex C-72	aqueous dispersion of an acrylic polymer	Rohm and Haas Company	45
Rhoplex HA-8	aqueous dispersion of an acrylic polymer	Rohm and Haas Company	46
Rhoplex HA-12	aqueous dispersion of an acrylic polymer	Rohm and Haas Company	45
Rhoplex K-3	aqueous dispersion of an acrylic polymer	Rohm and Haas Company	-
Uformite MM-46	melamine-formaldehyde resin	Rohm and Haas Company	-
Vinyl pyrrolidene/vinyl acetate copolymer Type I-535	solution of the copolymer in isopropanol	Antara Chemical Company	50

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[a] Active ingredients.

MATERIALS USED FOR DESIGN STUDIES

Aluminum zipper	A lightweight aluminum zipper made by Talon, Inc.
Elastic	$\frac{3}{8}$-inch elastic purchased locally from F. W. Woodworth and Company
Heat-sensitive tape with grippers	Made by Scovill Manufacturing Company, Inc.
Metal eyelets	Purchased locally from F. W. Woolworth and Company
Polyethylene tape	A pressure-sensitive tape made by Fasson Products, Inc.
Standard metal grippers	Purchased locally from F. W. Woolworth and Company
Velcro tape	Purchased locally from Pizitz Department Store
Zephry zipper	A monofilament nylon zipper made by Talon, Inc.

NONWOVEN FABRICS

Trade name	Source	Description	Binder	Percent binder	Weight, oz/yd^2
Barlinn Nonwoven Style No. RI-400 2425	Chicopee Manufacturing Company	50% cellulose acetate, 50% viscose rayon	Rhoplex	-	1.0
Barlinn Nonwoven Style No. S-450-DM-3011	Chicopee Manufacturing Company	100% viscose rayon	Viscose	-	1.0
Pellon Style No. 970W	Pellon Corporation	a	a	a	1.6
Pellon Style No. 717W	Pellon Corporation	a	a	a	1.3
Pellon Style No. 40W	Pellon Corporation	a	a	a	2.1
Pellon Style No. 901 Nat	Pellon Corporation	a	a	a	1.6
Pellon Style No. 30W	Pellon Corporation	a	a	a	1.5
Rayon nonwoven	Curlator Corporation	100% rayon, $1\frac{9}{16}$-inch, 3.0-denier fibers	none	none	2.0
Fabric 1	J. P. Stevens	40% 1.5 denier, 2.5-inch nylon, T-201[b], semi-dull; 40% 1.5 denier, 2-inch rayon, Narcon[d] No. 2, bright	Rhoplex B-15[e]	20.0	3.0
Fabric 3	J. P. Stevens	40% 2.3-denier, 2-inch nylon, T-402[c], semi-dull; 40% 1.5-denier, 2-inch rayon, Narcon No. 2, bright	Rhoplex B-15[e]	20.0	3.0
Fabric 5	J. P. Stevens	47.5% 1.5 denier, 2.5-inch nylon, T-201[b], semi-dull; 47.5% 1.5 denier, 2-inch rayon, Narcon No.[d] 2, bright	Rhoplex B-15[e]	5.0	2.0
Fabric 6	J. P. Stevens	95% rayon web, 1.5 denier Narcon No. 2[d]	Rhoplex B-15[e]	5.0	1.4
Fabric 7	J. P. Stevens	95% 1.5 denier, 2-inch rayon, Narcon No. 2[d] bright	Rhoplex B-15[e]	5.0	2.0
Fabric 8	J. P. Stevens	92% 1.5-denier, 2-inch, T-402[c], semi-dull nylon	Rhoplex B-15[e]	8.0	
Fabric 9	J. P. Stevens	88.5%, 1.5-denier, 2.5-inch nylon, T-201[b], semi-dull	Rhoplex B-15[e]	11.5	2.2
Rayon nonwoven	J. P. Stevens	1.5-denier, 2-inch bright, Narcon No. 2[d] rayon fibers	none	none	

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[a] Unable to obtain information from Pellon Corporation.

[b] Normal tenacity, heat set nylon.

[c] High tenacity, no-crimp nylon.

[d] High tenacity rayon.

[e] An acrylic binder.

OIL REPELLENTS AND WATER REPELLENTS

Aquapel	A water repellent of alkyl ketone dimers (100% solids) from Hercules Powder Company, Inc.
Aridex C Concentrate	A 60% dispersion of wax and aluminum soap, from E. I. du Pont de Nemours and Company
FC-154	Nonionic emulsion of a fluorocarbon (30% solids), from Minnesota Mining and Manufacturing Company
FC-208 (Textile Chemical)	Non-ionic emulsion of a fluorocarbon resin (28% solids) from Minnesota Mining and Manufacturing Company
FC-805 (Paper Chemical)	30% solution of the chrome complex of perfluoroctanoic acid in isopropanol, from Minnesota Mining and Manufacturing Company
L-1100 and L-1138	Fluoro-organic chemicals, from Minnesota Mining and Manufacturing Company
Norane R	Long chain pyridinium compound, from Warwick Chemical Division, Sun Chemical Corporation
Permel B	40% dispersion of a melamine resin, from American Cyanamid Company
Phobotex FTC	Synthetic resin water repellent from Ciba Company
Quilon	Werner-Type chromium complex of fatty acid (30% solids) in isopropanol, from E. I. du Pont de Nemours and Company, Inc.
Velan NW	Long-chain pyridinium compound from I. C. I. Organics, Inc.
Zelan AP Paste	A pyridinium compound (90% solids), from E. I. du Pont de Nemours and Company, Inc.
Zepel B	Fluorocarbon (14% solids), from E. I. du Pont de Nemours and Company, Inc.

* An acrylic binder.

PAPERS

Name	Manufacturer	General Description	Reinforcing agent
A. Miscellaneous Papers			
1. Flexrope 8235	John A. Manning Paper Company	bleached kraft rope fiber paper	none
2. Flexrope 8345	John A. Manning Paper Company	bleached kraft rope-fiber paper, uncalendered	none
3. Rotoform	Hollingsworth and Vose Company		none
4. Bleached filter crepe paper No. 35	Hollingsworth and Vose Company	all-wood filter paper with high wet strength	none
5. Wet strength cover stock	Hollingsworth and Vose Company	unbleached crepe filter paper with high wet strength	none
B. Reinforced Papers			
1. Creped paper	Mosinee Paper Mills	unbleached, crepe kraft paper reinforced with rayon scrim; paper layer on one side of scrim is much thicker than on the other side	bonded, continuous filament rayon scrim of $\frac{1}{2}$-inch mesh
2. Kaycel 100	Kimberly-Clark Corporation	cellulose wadding reinforced with nylon strands	nonwoven web composed of 6 x 5 strands/in. of 100-denier nylon yarn
3. Kaycel 101-1	Kimberly-Clark Corporation	cellulose wadding reinforced with nylon strands; has flame retardant treatment; contains about 19% binder	nonwoven web of 6 x 5 strands/in. of 100-denier multi-filament nylon yarn
4. Kaycel 101-3	Kimberly-Clark Corporation	cellulose wadding reinforced with nylon strands; has water repellent treatment; contains about 20% binder	nonwoven web composed of 6 x 5 strands/in. of 100-denier multi-filament nylon yarn
5. Kaycel RSR 8514	Kimberly-Clark Corporation	cellulose wadding reinforced with nylon strands; has Rhoplex abrasive resistant treatment and water repellent	nonwoven web of 6 x 5 strands/in. of 100-denier nylon yarn
6. Kaycel RSR 8525	Kimberly-Clark Corporation	cellulose wadding reinforced with nylon strands; has abrasive resistant treatment; contains 20% Rhoplex binder	nonwoven web containing 100-denier nylon in warp and 210 denier in fill, 9 x 5 strands/in.
7. Kaycel CWC-15-2	Kimberly-Clark Corporation	cellulose wadding reinforced with nylon strands; treated with 25% Rhoplex B-15 and overpadded with 3% FC-208	nonwoven web of 6 x 5 strands/in. of 100-denier nylon yarn
8. Chixel	Chicopee Manufacturing Corporation	paper reinforced with cotton gauze; poly(vinyl chloride) binder	cotton gauze
C. Laminated Papers			
1. Kaycel 100, polyethylene coated	Kimberly-Clark Corporation	cellulose wadding reinforced with nylon strands and coated with polyethylene; 0.8 mil polyethylene coating	nonwoven web of 6 x 5 strands/in. of 100-denier multi-filament nylon yarn
2. Disposable rain wear	Disposables, Inc.	polyethylene coated, nylon-reinforced paper	probably same as Kaycel 101-1
3. No-Wet Thru 7502	NWT Corporation	extra strength Mylar with facial tissue on both sides	
D. Synthetic Fiber Papers			
1. Masslin M-840-B	Chicopee Manufacturing Company	viscose fibers with a poly(vinyl acetate) binder	none
2. Masslin RI-750-2209	Chicopee Manufacturing Company	acetate viscose fibers with an acrylic binder	none
3. Masslin SI-1300-2110	Chicopee Manufacturing Company	-	none
4. Havotex	Hollingsworth and Vose Company	nylon, polyester, and cellulose containing an acrylic binder	none
5. Dacron	Kimberly-Clark Corporation	Dacron textryl paper	none

PIGMENTS

Trade name	Source
Green B Paste, GW-744-P	E. I. du Pont de Nemours & Company, Inc.
Lithosol-Fast Yellow HV Paste	E. I. du Pont de Nemours & Company, Inc.
Lithosol-Red CSP Paste	E. I. du Pont de Nemours & Company, Inc.
Multisperse Black C 11-991	Sherwin-Williams Company
Multisperse Yellow LC 12-960	Sherwin-Williams Company
Multisperse Yellow M 12-961	Sherwin-Williams Company
W-308, Titanium Dispersion	Harshaw Chemical Company
W-1840, Organic Yellow Dispersion	Harshaw Chemical Company
W-2080, Dinitraniline Orange Dispersion	Harshaw Chemical Company
W-7017 R, Carbon Black Dispersion	Harshaw Chemical Company

PLASTICIZERS AND SOFTENERS

Aliquat 336	A tricapryl monoethyl ammonium chloride from General Mills, Inc.
Carbitol	A diethylene glycol monoethyl ether from Carbide and Carbon Chemicals Company
Celluflex FR-2	Tris(2, 3-dichloropropyl)phosphate from Celanese Corporation of America
C_{20} "oxo" alcohol	An "oxo" alcohol from Enjay Company
Epolene E	A polyethylene (100% solids) prepared by Eastman Chemical Products
Good-rite Plasticizer GP	Dioctyl phthalate plasticizer made by B. F. Goodrich Chemical Company
Santicizer 141	An alkyl aryl phosphate from Monsanto Chemical Company
Syl-Soft 12	Silicone-based softener (30% solids) made by Dow Corning Corporation
Triethylene glycol	A glycol from Carbide Carbon Chemical Company

THICKENERS AND STABILIZERS

Carbopol	Synthetic gel forming polymer from B. F. Goodrich Chemical Company
Guar Gum	Plant mucilage from General Mills, Inc.
Gum Arabic	Plant gum from Uni-Gum Division of T. M. Duché and Sons, Inc.
Gum Tragacanth	Plant gum from Central Scientific Company
Methocel	4000 cps grade, Dow Chemical Company
Protovac PV 432	Casein made by Borden Chemical Company
Sodium Alginate	Seaweed colloid from Matheson, Coleman, and Bell Division of the Matheson Company

WOVEN FABRICS

Material	Fiber content	Source	Weight, oz/yd[a]	Construction Ends/in.	Construction Picks/in.
Nylon chiffon	100% nylon	Sears Roebuck and Company	1.1	110	92
Organdy	100% Egyptian combed cotton	Sears Roebuck and Company	1.5	87	66
Acetate taffeta[a]	100% acetate	U. S. Natick Laboratories	2.0[b]		
Nylon	100% nylon	Unknown	2.1		
Batiste	100% combed cotton	Sears Roebuck and Company	2.2	86	69
Silk	100% silk	Burger-Phillips (local)	2.3		
Pique	100% Dacron polyester	Sears Roebuck and Company	2.5	107	83
Nylon Style 1181	210 denier warp and filling nylon	Burlington Fabric Industries	2.5		
Dacron Style 1295	100% Dacron	Burlington Fabric Industries	2.5		
Crepe	73% arnel triacetate, 27% nylon	Sears Roebuck and Company	2.9	165	92
Pima cotton broadcloth	100% pima cotton	Famous Cotton Bowl (local)	3.0		
Cotton lawn	100% cotton	Test Fabrics, Inc.	3.1		
Cotton chintz	100% cotton	Lovemans (local)	3.2		
Linen	100% Irish linen (imported)	Sears Roebuck and Company	3.3	69	97
Cotton print cloth	100% cotton	Test Fabrics, Inc.	3.3		
Percale	100% cotton	Sears Roebuck and Company	3.4	71	57
Cotton chiffon	100% pima cotton	Sears Roebuck and Company	3.4	125	78
Cotton broadcloth	100% cotton	Famous Cotton Bowl	3.5		
Cotton broadcloth	100% cotton	U. S. Natick Laboratories	3.5	115	56
Cotton sheeting, OD	100% cotton	U. S. Natick Laboratories	4.0	48	48
Cotton sheeting, No. 2	100% cotton	Clifton Manufacturing Company	4.0	58	62
Dacron-cotton		Burger-Phillips (local)	4.2		
Nylon oxford	100% nylon	U. S. Natick Laboratories	4.4		
Cotton sheeting No. 1	100% cotton	Clifton Manufacturing Company	4.5	63	70
Polypropylene	100% polypropylene	Burlington Industries, Inc.	4.8	56	43
Textured nylon	70-denier textured nylon in warp, 140-denier nylon yarn in filling	Georgia Institute of Technology	5.0	190	105
Cotton-nylon oxford	cotton warp, nylon filling	U. S. Natick Laboratories	5.0	105	68
Cotton oxford	100% cotton	U. S. Natick Laboratories	5.2		
Cotton sheeting No. 3	100% cotton	Test Fabrics, Inc	5.3	53	47
Cotton poplin	100% cotton	U. S. Natick Laboratories	5.5	116	51
Cotton oxford No. 26	100% cotton	U. S. Natick Laboratories	6.2	196	83
Cotton May Duck 185 No. 5	100% cotton	Famous Cotton Bowl (local)	6.4	92	30
Cotton oxford No. 42	100% cotton	U. S. Natick Laboratories	6.4	197	90
Cotton oxford No. 38	100% cotton	U. S. Natick Laboratories	6.6	166	81
Cotton oxford No. 30	100% cotton	U. S. Natick Laboratories	6.8	194	71
Cotton sheeting	100% cotton	U. S. Natick Laboratories	7.0		
Cotton drill	100% cotton	Liberty Trouser Company (local)	7.1		
Cotton oxford No. 46	100% cotton	U. S. Natick Laboratories	7.3	194	82
Cotton denim	100% cotton	Avondale Mills	7.4		
Duck, DF Enamel	100% cotton	Walton Cotton Mill Company	7.5		
Cotton Osnabury No. 4	100% cotton	Famous Cotton Bowl (local)	7.6	45	32
Wool	100% wool	Burger-Phillips (local)	7.8		
Cotton sateen	100% cotton	On hand	8.0		
Polypropylene	100% polypropylene	Unknown	8.2		
Cotton twill	100% cotton	Liberty Trouser Company (local)	8.4		
Cotton sateen	100% cotton	Clifton Manufacturing Company	8.5		
Cotton ticking	100% cotton	Famous Cotton Bowl (local)	8.8		
Cotton oxford No. 24	100% cotton	U. S. Natick Laboratories	8.8	144	70
Cotton oxford No. 37	100% cotton	U. S. Natick Laboratories	11.2	108	53
Cotton oxford No. 45	100% cotton	U. S. Natick Laboratories	11.4	116	50
Cotton oxford No. 29	100% cotton	U. S. Natick Laboratories	11.5	115	50
Cotton oxford No. 41	100% cotton	U. S. Natick Laboratories	12.0	97	47
Cotton oxford No. 33	100% cotton	U. S. Natick Laboratories	12.3	113	40

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[a] Calendered.

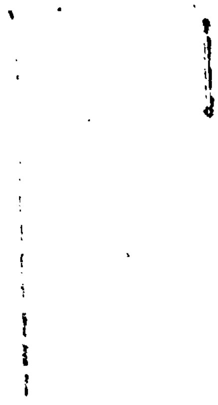
[b] Weight before calendered.

YARNS

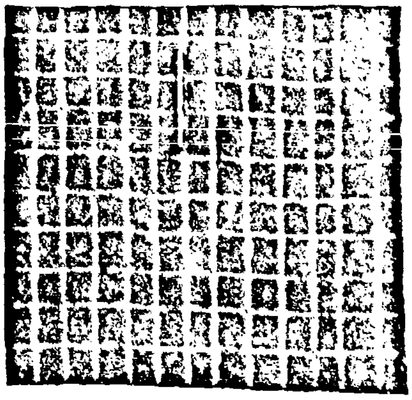
Cellulose acetate	100-denier, 40 filament, 2-Z twist, Type 4W dull made by Celanese Fibers Company
Dacron	100-denier, multifilament, Type Dacron yarn made by E. I. du Pont de Nemours and Company, Inc.
Nylons	100-denier, 34-filament, 0.5-Z twist, Type 680 and 200-denier, 34-filament, 0.75-Z twist, Type 300 nylon made by E. I. du Pont de Nemours and Company, Inc.
Polyethylene	170-denier, monofilament polyethylene made by Reeves Plastics, Inc.
Rayon	100-denier, 60-filament, 2-Z twist, Type 11 dull made by Celanese Fibers Company
Rovana	400-denier Saran yarn, which is approximately 20-25 mils in width, made by the Dow Chemical Company

APPENDIX C

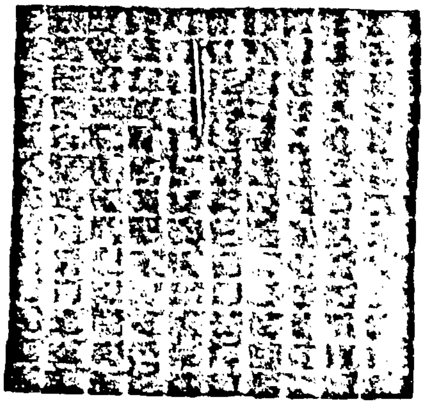
SAMPLES OF PLANT PRODUCED EXPERIMENTAL PAPERS



Experimental Paper No. 2-2-62



Experimental Paper No. 6-21-62R



Experimental Paper No. 6-21-62GCD

APPENDIX D

MATERIAL SUPPLIED TO U. S. ARMY NATICK LABORATORIES

200 yards of Experimental Paper No. 1-8-62; an undyed, scrim-reinforced nylon-wood pulp paper treated with Rhoplex B-15 and FC-208, prepared on pilot-plant equipment.

1700 yards of Experimental Paper No. 2-2-62, an undyed, scrim-reinforced nylon-wood pulp paper treated with Rhoplex B-15 and FC-208, prepared on plant production equipment.

1000 yards of Experimental Paper No. 6-21-62R; a scrim reinforced nylon-wood pulp paper, dyed OD and treated with Rhoplex HA-12 and FC-208.

1000 yards of Experimental Paper No. 6-21-62GCD; a scrim-reinforced nylon-wood pulp paper, dyed OD and treated with Geon 577, antimony trioxide, and FC-208.

100 yards of Experimental Nonwoven Fabric No. 10-30-62R; a nonwoven fabric containing 60% rayon fibers and 40% Rhoplex HA-8/Rhoplex HA-12 mixture (1:1 solids ratio) and treated with Flameproof 290B and FC-208.

100 yards of Experimental Nonwoven Fabric No. 10-30-62N; a nonwoven fabric containing 60% nylon fibers and 40% Geon 351 and treated with Flameproof 290B and FC-208.

100 yards of E-18 Gas Aerosol Filter containing glass, viscose, and vinyon fibers.

500 yards of 1.8 oz/yd^2 Fortisan fabric treated with a S-330/Hycar 2671 mixture.

500 yards of Kyron S/403 nonwoven fabric.

APPENDIX D (continued)

550 yards of rayon nonwoven fabric with nylon scrim needle punched to one side and treated with carbon/Hycar 2000 X 83.

550 yards of rayon nonwoven fabric with a nylon scrim needle punched to both sides and treated with carbon/Hycar 2600 X 83.

300 yards of polyurethane foam with nylon tricot fabric flame bonded to one side of the foam and treated with carbon/Hycar 2600 X 83.

200 yards of untreated polyurethane foam with nylon tricot fabric flame bonded to one side of the foam.

500 yards of untreated polyurethane foam with nylon tricot fabric flame bonded to both sides of the foam.