TECHNICAL BULLETIN

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ISP 1007

WATER AND STAIN REPELLENT FINISHING OF COTTON FABRICS

This bulletin is sponsored by the Importer Support Program and written to address the technical needs of product sourcers.

TABLE OF CONTENTS

INTRODUCTION

Fluorochemical water/stain repellent finishes can provide durable liquid repellence (water and oil) without compromising the natural feel of cotton. With proper chemical treatment and selection of fabric construction, garments can be produced that provide a host of benefits to the wearer, such as staying clean longer, faster drying, and protection from rain and snow.

Water/stain repellent cotton fabrics can be used for a variety of end uses such as outerwear, where the focus is on a high degree of water repellency, and general wearing apparel such as casual pants, where the focus is more on stain resistance. Other common end uses for fluorochemical repellents include upholstery, rugs, and carpet

This technical bulletin describes current fluorochemical products and finishing procedures used to produce 100% cotton water and stain repellent fabrics for end uses such as outerwear and general wearing apparel.

STAIN REPELLENCY

The development of stain repellent general wearing apparel has taken place in response to the consumers' desire for easy-care garments.

Note that this technical bulletin relates to water repellent and stain *repellent* finishes and does not discuss soil *release* or combination repellent/release finishes or properties.

Stain Repellent (or Resistant) Finish: Prevents water and/or oils from penetrating the fabric causing potential aqueous and oily stains to bead up and roll off. Test methods used for evaluation include Oil Repellency (AATCC 118) for oily stain resistance and the Isopropanol/Water Drop test for aqueous stain resistance.

Stain/Soil Release Finish: Enhances the ability of a fabric to release stains during laundering. For a release finish, liquids may not bead up, but usually soak into the fabric. Soil Release test (AATCC 130) is used for evaluation.

Combination Repellent/Release Finish: Provides limited stain repellency plus soil release with the objective of overall stain management.

TEST METHODS -- Stain Repellency

Oil Repellency (AATCC 118): Measures the resistance to wetting by a series of hydrocarbon test liquids with varying surface tensions (oily liquids). The oil repellency grade is the highest numbered test liquid that does not wet the fabric surface.

- Oils are numbered 1 – 8 with #8 being the highest (most oil repellent) rating. Many specifications require a 3 rating after multiple launderings.

Isopropanol/Water Drop Test (proposed AATCC test method): Measures the resistance to wetting by aqueous liquids (aqueous stain resistance) using a series of isopropanol/water mixtures with varying surface tensions.

- Rating of 10 (20% water, 80% isopropanol) is highest (most repellent). The minimum acceptable rating is typically 4 or 5 after multiple launderings.

WATER REPELLENCY

Water Repellent Finish: Prevents water from wetting the fabric. Test methods used for evaluation vary widely in severity and include the Spray test (AATCC 22), Rain test (AATCC 35), Hydrostatic Pressure test (AATCC 127), Bundesmann rain/shower test (ISO 9865), etc. The test methods chosen depend on the degree of water repellency that is desired.

Water Repellent Fabric: Prevents water from wetting or penetrating through the fabric. It can be broken down into various degrees of water repellency that depend heavily on fabric construction. For example, a knit fabric treated with a water repellent will stay dry when sprayed with water; however, due to the loose structure of the knit fabric, water will penetrate through the fabric. A waterproof fabric prevents all water from penetrating the fabric.

Fabric Construction

While the chemical finishes used for both applications are very similar, the key difference between outerwear (rainwear) and general apparel (casual pants) applications is the requirement to pass the rain test (AATCC 35). Performance in the rain test depends heavily on fabric construction and not only on fabric finish.

A regular cotton 3/1 twill fabric (7.5 oz/yd^2), which is typically used for casual pants, does not have a tight enough construction to pass the rain test. However, a heavier cotton fabric such as a 9.0-10.0 oz/yd^2 canvas does have a very tight construction and can perform successfully in the rain test with proper treatment. Another alternative is to use a specialty fabric that has very fine yarns and a very tight weave.

TEST METHODS -- Water Repellency

Spray Test (AATCC 22): Measures resistance of fabric to surface wetting under mild water impact.

- Does not measure water penetration through the fabric, only the fabric surface is visually rated. Widely used as a quick, easy, inexpensive screening test. Highest rating is 100; 70 is the lowest acceptable rating required for many repellent fabrics.

Rain Test (AATCC 35): Penetration of water through the fabric is tested by placing a blotter of known weight behind the fabric sample, spraying with water for a specified time, and re-weighing the blotter. The intensity of the water impact can be adjusted by using a higher column of water.

- For a garment to be considered rainwear by U.S. Customs, the fabric must pass the rain test with less than 1.0 gram of water penetrating the fabric when sprayed for 2 minutes using a 2-foot column of water.
- The highest test level generally used for apparel is 3 feet for 5 minutes.
- Passing the test depends heavily on fabric construction (tightness).

Bundesmann Rain/Shower Test (ISO 9865): Subjects fabric to an artificial rain shower, rates the specimens visually for surface wetting, measures the water absorbed by the specimen, and measures the amount of water that penetrates through the specimen.

- This is a severe test of water repellency. There are very few Bundesmann testers in the U.S., as the test is mainly used in Europe.

Hydrostatic Pressure Test (AATCC 127): Fabrics are subjected to increasing water (hydrostatic) pressure until 3 points of leakage appear.

- Severe test of waterproofness used for high-tech fabrics.

TEST METHODS -- Breathability

Water repellent fabrics must be tight enough to prevent water from penetrating the fabric; however, in order to provide comfort to the wearer, they must be breathable, i.e. they must allow moisture vapor (or air) to pass through the fabric.

Air Permeability (Frazier) (ASTM D737): Measures the rate of airflow passing perpendicularly through a fabric.

- Can be interpreted as breathability or wind resistance. Results are in cubic feet/minute through 1 foot^2 of fabric ($ft^3/min/ft^2$).

Moisture Vapor Transmission Rate (MVTR) (ASTM E96, procedure B): Measures the rate of moisture vapor diffusion through fabric using the Simple Dish method.

- Procedure must be specified. The most commonly used procedure is Procedure B, the upright cup, water method at 73.4°F (23°C); results are in grams/square meter/24 hours (g/m^2/24 hrs).

PREPARATION FOR FINISHING

To achieve the best durability of the water/stain repellent finish, proper preparation of the fabric is essential. Auxiliary residues on the fabric such as pretreatment agents, sizes, surfactants, or dyeing auxiliaries can impair water and oil repellent performance.

Fabric pH, residual alkalinity, and water and solvent extractables should be tested before finishing to check for proper preparation. Recommended fabric properties are listed below:

Fabric pH (AATCC 81) should be 5.5 – 7.5 (some chemical suppliers recommend pH of 5.5 – 6.5).
Percent Alkalinity (AATCC 144) should be less than 0.05% NaOH.
Water extractables (AATCC 97) should be less than 0.4%.
Solvent extractables (AATCC 97) should be less than 0.1%.
Drop absorbency (AATCC 79) should be immediate.

A spot test[1] can be done to ensure that there is no size on the fabric, and a foaming test[2] can be done to check for residual surfactants.

OTHER CONSIDERATIONS IN FINISHING

The pH of the finishing bath should be between 4 and 5 for most products. It can be adjusted with acetic acid (56%) as necessary.

Mixing and processing equipment must be kept free of any silicone contaminant. In general, the presence of silicone severely affects oil repellency.

If foaming problems are encountered, a non-silicone foam control agent may be used.

DRY/CURE CONDITIONS

Drying can be accomplished using regular textile equipment such as a tenter frame at a temperature of 195°-250°F (90°-121°C). Fabric should be "bone" dry before curing.

Fluorochemical repellent finishes require a heat "cure" to develop their optimum repellent properties. If the fabric is not cured properly, durability of the finish can suffer. The manufacturer's recommendations for curing should be checked for the specific fluorochemical that is used. Some require a minimum cure temperature of 340°F (171°C) for 1 minute, while others recommend curing for 3 minutes at 300°F (150°C) or 30-40 seconds at 338-356°F (170°-180°C). Higher curing temperatures can have a highly advantageous effect on durability.

[1] See Livengood, Charles D. "Spot test for identification of warp sizes on fabrics." *Textile Industries.* September 1983, pp. 114-116.
[2] See 3M Application Guide, April 2003.

FORMULATIONS

A fluorochemical water/stain repellent can be used in conjunction with various other chemicals detailed in the following:

- Crosslinker
  - Some fluorochemicals require a separate crosslinker to provide durability of the finish, while others have crosslinking agents built in and do not require a separate crosslinker.

- Extender
  - An extender is a less expensive aliphatic or wax water repellent that is used to boost performance and help reduce the amount of fluorochemical needed.

- Non-rewetting, wetting agent
  - A fugitive wetting agent should be used when necessary to achieve adequate wetting of the fabric and proper penetration of the finish. A non-rewetting, wetting agent will then evaporate or "flash off" during curing. If a regular wetting agent is used, it may remain on the fabric after curing and interfere with water repellency.

- Softener
  - If a softener is used, it must be compatible with the fluorochemical. Silicone softeners must be chosen carefully, so they do not interfere with oil repellency. Consult the fluorochemical manufacturer for a compatible softener.

- Glyoxal (DMDHEU) resin
  - If wrinkle resistance is desired, a DMDHEU resin may be added. The additional crosslinking that a resin provides may also improve durability for some fluorochemicals.

- Catalyst based on magnesium chloride ($MgCl_2$)
  - Use as necessary in conjunction with the glyoxal (DMDHEU) resin.

A suggested formulation for a woven fabric is shown below (percent on weight of bath):

6% - 8%	Fluorochemical repellent
5%	Extender (optional)
0.2%	Non-rewetting, wetting agent
5%	Glyoxal (DMDHEU) resin
1.5%	$MgCl_2$ catalyst

For a regular 3/1 cotton twill, 70% wet pick-up is typical. For a 10 oz. cotton canvas, wet pick-up can be 55%-60%.

TEST RESULTS

Stain Repellency

Test results are shown below for stain repellent cotton twill subjected to 5, 15, and 30 home launderings. The data is for a sample treated with 8% fluorochemical repellent, 5% DMDHEU resin, and 1.5% $MgCl_2$ catalyst with 70% wet pick-up. Acceptable performance is achieved in the spray, oil repellency, and isopropanol/water drop tests even after 30 home launderings. Ironing can help regenerate the finish and boost performance.

	Unlaundered	5 HLTD[1]	15 HLTD	30 HLTD	30 HLTD + ironing
Spray test (AATCC 22)[2]	100	95	85	70	80
Oil Repellency (AATCC 118)[3]	7.0	6.0	6.0	4.5	6.0
Isopropanol/Water Drop Test[4]	10	10	10	7.5	8.0

[1] "HLTD": Home laundering @ 105°F using standard AATCC detergent, and tumble dry for 30 minutes.
[2] AATCC 22 allows intermediate ratings (such as 85 and 95) to be used for samples that fall in between the standard ratings. The lowest acceptable rating is 70.
[3] Minimum acceptable oil repellency rating is typically 3.0.
[4] Minimum acceptable rating is typically 4.0-5.0.

Water Repellency

As shown in the table below, a 10.0 oz. cotton canvas treated with the suggested formulation mentioned previously can pass the rain test (AATCC 35) at the highest level typically used for apparel, 3 feet of water pressure for 5 minutes, even after 10 home launderings. Spray test ratings and Hydrostatic pressure test results are also shown in the table.

Sample - 100% cotton, 10.0 oz. canvas treated with fluorochemical water repellent	Unlaundered	After 10 HLTD[1]
Spray Test (AATCC 22) rating[2]	100	80-85
Rain Test (AATCC 35) Blotter Weight Difference of less than 1.0 g = Pass Level: 3 feet for 5 minutes "storm"	0.2 g Pass	0.2 g Pass
Hydrostatic Pressure test (AATCC 127) – Suter[3]	54.5 cm	N/A

[1] "HLTD": Home laundering @ 105°F using standard AATCC detergent, and tumble dry for 30 minutes.
[2] Lowest acceptable spray rating is 70. Note that spray test ratings do not necessarily correspond to rain test results because the spray test only rates the surface of the fabric while the rain test measures the amount of water that passes through the fabric.
[3] Testing performed by SGS U.S. Testing Company, Inc., Fairfield, NJ.

Drying Time

In addition to providing water and oil repellency, treatment with a fluorochemical water/stain repellent produces a fabric that dries significantly faster than an untreated fabric. The table below compares an untreated cotton twill, a wrinkle-resistant resin-treated cotton twill, and two water/stain repellent cotton twills in drying time tests. As shown in the table, the fluorochemical treated samples had lower wet pick-ups (absorbed less water) than the untreated samples and therefore had faster drying times.

Samples - 100% cotton twill	Average Wet Pick-up (%)[1]	Average Drying Time (min.)[1]
No Finish	76.1%	238
Wrinkle resistant, DMDHEU resin-treated	56.4%	147
Fluorochemical repellent A, +DMDHEU resin	27.2%	76
Fluorochemical repellent B, +DMDHEU resin	24.4%	69

[1] Samples were wet-out by rotating for 20 minutes using 2 L de-ionized water in the Tumble Jar Dynamic Absorption tester along with 9, 6"x6" pieces of twill ballast, extracted in the Quickwash for 10 seconds, then dried flat on a raised screen at 70°F & 65% RH.

EFFECT OF FLUOROCHEMICAL FINISHES ON COMFORT

Fluorochemical water/stain repellents do not change the natural breathability of cotton fabrics. As shown in the table below, air permeability and moisture vapor transmission rate are only slightly affected by fluorochemical treatment.

Sample – Regular 3/1 Cotton Twill	Frazier Air Permeability (ASTM D737)	Average Moisture Vapor Transmission Rate (MVTR), ASTM E96, Procedure B*
No Finish	20.0 $ft^3/min./ft^2$	810.9 $grams/m^2/24$ hours
Treated with 6% Fluorochemical Repellent, + DMDHEU resin	20.2 $ft^3/min./ft^2$	771.1 $grams/m^2/24$ hours

** Testing performed by NCSU, T-PACC, Raleigh, NC.*

Water repellent cotton canvas has greater breathability than a typical synthetic jacket that claims to be breathable as shown below.

Sample	Average Moisture Vapor Transmission Rate (MVTR), ASTM E96, Procedure B
10 oz. cotton canvas, treated with 10% fluorochemical water repellent	673.6 $grams/m^2/24$ hours
High-tech synthetic jacket claiming breathability	564.1 $grams/m^2/24$ hours

** Testing performed by SGS U.S. Testing Company, Inc., Fairfield, NJ.*

CONSUMER PRACTICES

For the best performance of fluorochemical treated fabrics after multiple launderings, several laundering recommendations should be emphasized to consumers.

The use of liquid fabric softeners or dryer sheets should be avoided, as they can interfere with water and oil repellency.

If fabrics are allowed to air dry, the fluorochemical finish may not be properly regenerated; therefore, it is important for consumers to promptly move garments from the washer to the dryer. (Some fluorochemical repellents are designed to perform after air drying and are referred to as Laundry-Air Dry or LAD; however, tumble drying is still best for optimal repellency.)

If performance decreases after many launderings, ironing can often help rejuvenate the finish. The heat from tumble drying or ironing helps regenerate water/stain repellency by reorienting the fluorochemical chains. Some retailers/suppliers recommend ironing after every fifth wash for optimal performance. An extra rinse to make sure the detergent is thoroughly rinsed off can also help to restore performance.

Care should also be taken when a stain occurs on a stain repellent fabric. Liquid stains bead up and roll off or can be gently "wicked" off with an absorbent towel; however, semi-solid stains, such as ketchup, mustard, etc., can be more difficult to remove. If a semi-solid stain occurs, the fabric should be blotted gently in a roll-up-and-swipe motion with an absorbent towel, taking care not to grind the stain further into the fabric.

CONCLUSIONS

Fluorochemical water/stain repellents can provide value-added benefits to 100% cotton fabrics.

For general wearing apparel such as casual pants, a wide variety of fabrics, including looser wovens and knits, can be used successfully to achieve durable stain repellency.

For end uses such as outerwear and rainwear, passing the rain test is required, which severely limits the fabrics that can be used to those with tighter constructions. For technical outerwear, tests more severe than the rain test may be required, such as the Bundesmann and the Hydrostatic Pressure test.

CHEMICAL SOURCES (in alphabetical order)

Bayer Chemicals
100 Bayer Road, Building 14
Pittsburgh, PA 15205-9741

Ciba Specialty Chemicals, Corp.
4050 Premier Drive / 27265
P.O. Box 2678
High Point, NC 27261-2678

Clariant Corporation
4331 Chesapeake Drive
Charlotte, NC 28216

Cognis Corporation
4900 Este Avenue
Cincinnati, OH 45232

Mitsubishi International Corporation (MIC)
Specialty Chemicals, Inc.
520 Madison Avenue
New York, NY 10022

Noveon, Inc.
9911 Brecksville Rd.
Cleveland, OH 44141-3247

The chemicals listed above are those used by Cotton Incorporated. Products from other suppliers may also be satisfactory.

Importer Support Program

The Cotton Board and Cotton Incorporated are funded by U.S. upland cotton growers and importers of cotton and cotton products (this includes raw cotton, piece goods, and finished apparel). A percentage of the importer funds are devoted for importer specific programs organized under the Importer Support Program. Examples of projects funded from this fund include training schools, educational programs, focus groups, economic meetings, and research initiatives.

Selected technical issues have been identified by importer members as relevant to their business. This report is a condensed, less technical report of those issues intended to provide the reader with basic, yet useful information on the topic.

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