Finishes in Textiles: Identification

Developed in 1959 by AATCC Committee RR45; revised 1961, 1962, 1965, 1987; reaffirmed 1969, 1973, 1977, 1985, 2002, 2007; editorially revised 1974; editorially revised and reaffirmed 1992, 1997.

1. Purpose and Scope

1.1 This test method gives guidelines for qualitative identification of various finish components present on textile fabrics, yarns or fibers.

1.2 The identification scheme may involve any or all of the following approaches:

1.2.1 Sequential solvent extractions followed by identification of extracts by infrared spectroscopy (IR), gas chromatography (GC), high performance liquid chromatography (HPLC), thin layer chromatography (TLC), nuclear magnetic resonance spectroscopy (NMR) or other instrumental or wet-chemical methods.

1.2.2 Direct measure of elemental or chemical species on fabric by X-ray fluorescence spectroscopy, infrared reflectance spectroscopy, furnace atomic absorption spectroscopy, and other instrumental or wet-chemical analysis methods.

1.2.3 Identification of specific finishing components by chemical spot tests on the textile or extracts from textiles.

2. Uses and Limitations

2.1 This test method is a flexible set of guidelines for identification of textile finishes. Appropriate adjustments and modifications will be needed as finishing chemicals change and as new analytical test methods are developed.

2.2 Any chemical which is on the textile prior to finishing may be present on the finished fabric and could be removed and/or detected as finish. Warp sizes, [e.g., starches, acrylics, waxes, polyesters, poly(vinyl alcohol)], dyes, dye fixatives, binders, spin finishes, natural gums, sugars, optical brighteners, and processing chemicals (e.g., surfactants, bleach stabilizers, dye carriers, and oils) may be present by design or unintentionally. A working knowledge of these chemicals is needed to properly detect and identify them. Where possible, supplier should be consulted for further information.

3. Terminology

3.1 **chemical finish,** n.—chemical material other than colorants and residual processing chemicals added to textiles to impart desired functional or aesthetic properties to the textile product.

NOTE: Chemical finish will hereafter be referred to as finish.

4. Safety Precautions

NOTE: These safety precautions are for information purposes only. The precautions are ancillary to the testing procedures and are not intended to be all inclusive. It is the user's responsibility to use safe and proper techniques in handling materials in this test method. Manufacturers MUST be consulted for specific details such as material safety data sheets and other manufacturer's recommendations. All OSHA standards and rules must also be consulted and followed.

4.1 Good laboratory practices should be followed. Wear safety glasses in all laboratory areas.

4.2 Use chemical goggles or face shield, impervious gloves and an impervious apron during dispensing and mixing of alkalis, acids and organic solvents. Concentrated acids should be handled only in an adequately ventilated laboratory hood. CAUTION: Always add acid to water.

4.3 Special precautions must be observed when using perchloric acid. All work must be done in an exhaust hood made of non-combustible material. Frequent wash down of the exhaust system is recommended as accumulated perchlorate combinations are often explosive. Addition of dehydrating agents, unless controlled, will lead to the anhydrous acid which is unstable. Care must be taken in handling perchloric acid. Use eye and face protection, and flush any spill or splash to the skin or eyes with water immediately.

4.4 Hexane and methanol are flammable liquids and should be stored in the laboratory only in small containers away from heat, open flames and sparks. These chemicals should not be used near an open flame.

4.5 Carry out reflux procedure in a well ventilated hood with an electrical heater or a water bath as the heating source. Use chemical goggles or face shield, impervious gloves and an impervious apron when handling organic solvents.

4.6 An eyewash/safety shower, organic vapor respirator and a self-contained breathing apparatus should be located nearby for emergency use.

4.7 Care should be taken in handling hot weighing bottles and crucibles. Severe burns can result from skin contact.

4.8 Manufacturer's safety recommendations should be followed when operating laboratory testing equipment.

4.9 Exposure to chemicals used in this procedure must be controlled at or below levels set by governmental authorities [e.g., Occupational Safety and Health Administration's (OSHA) permissible exposure limits (PEL) as found in 29 CFR 1910.1000 of January 1, 1989]. In addition, the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) comprised of time weighted averages (TLV-TWA), short term exposure limits (TLV-STEL) and ceiling limits (TLV-C) are recommended as a general guide for air contaminant exposure which should be met (see 14.1).

5. Sample Preparation

5.1 Textile samples should be dried at 105 ± 1°C and desiccated to constant weight prior to weighing for subsequent extractions.

6. Solvent Extraction Procedures

6.1 Extraction with different solvents is intended to remove as many finishing chemicals as possible in a sequential order. The extraction scheme presented here (see Table I) was chosen on the basis of solvent polarity, solubility, volatility, economy and safety.

6.2 Changes in chemical finishes, safety considerations or personal preferences may dictate the use of other solvents. It is the responsibility of the user to determine which finish types may be removed by different solvents.

6.3 Some finishes may not be soluble in any solvent. An alternate method for insoluble finishes such as fully cross-linked polymers [e.g., some acrylics, polyurethanes, silicones and poly(vinyl acetates)] would be to dissolve all of the fibrous material with a suitable solvent, leaving the residue of finish for further analysis (see AATCC Method 20, Fiber Analysis: Qualitative, Table V).

6.4 Procedure. A weighed textile sample (1-10 g depending on the size of the extractor) is extracted in sequence by the solvents in Table I, using Soxhlet reflux or beaker extractions depending on equipment availability. Extraction times may range from 45 min to several hours

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Table I

Group	Solvent	Polarity Index*	Typical Finishing Chemicals Removed
1	Hexane	0.1	Oils, waxes, softeners, silicones
2	1,1,1-Trichloroethane	1.0	Small amounts of unfixed polymers, polyester resins, acrylics, polyurethanes, poly(vinyl acetates)
3	Methanol	5.1	Unfixed cellulose reactants, organic salts, sulfonated organics
4	Water	10.2	Unfixed cellulose reactants, urea, linear starches, poly(vinyl alcohol)
5	0.1 *N* Hydrochloric acid	10.2	Fixed cellulose reactants, branched starches, inorganic salts

*Burdick and Jackson

NOTE: Some types of fibers may be partially dissolved by the solvents. Pre-checks on the fiber types (see AATCC Method 20) should be made to avoid errors.

depending on the boiling point, exchange rate and knowledge of the history of finish removal for the textile sample in question. The samples should be completely dried before beginning the next solvent in the sequence. After the extractions are complete, each solvent is filtered and evaporated or distilled leaving the residual finish extract. (The extract may be transferred to a weighing pan prior to complete dryness; drying can then be completed in an oven at 105 ± 1°C. Calculate the percent extract as follows:

Extract =

$$100 \times \frac{\text{Weight of Residue}}{\text{Weight of Original Fabric}}$$

NOTE: It may be useful to neutralize the acid extract with dropwise addition of dilute sodium hydroxide to avoid further degradation of the finish during evaporation. The quantitative results will reflect the presence of sodium chloride in the dried residue. In addition, contamination of the solution by sodium carbonate from the reaction of sodium hydroxide with atmospheric carbon dioxide may interfere with interpretation of subsequent infrared spectra.

The percent extract, coupled with subsequent identification, will be useful in distinguishing true finish components from residual non-finishing chemicals that may have been left on the fabric; e.g., natural waxes from softeners.

The extracted finish may be identified by one of the analytical techniques described below.

7. Infrared Spectroscopic Procedures

7.1 Infrared spectroscopy offers a very convenient way to identify extracted finish from textiles. The basis for infrared spectroscopy is the structural information about a compound that can be found from its infrared spectrum. Infrared absorption bands in the 4000 to 250 wavenumbers region result from specific functional groups in a molecule. These can be compared with spectra of finishes in published or personal libraries. Visual inspection by a trained analyst will quickly identify the general type of finish. Computerized search-and-match capabilities on many infrared systems will be helpful. For more complete information, including typical wavenumbers for comparison of spectra of textile materials, descriptions of newer techniques such as Fourier transform infrared spectroscopy (FTIR), attenuated total reflectance spectroscopy (ATR) and primary references, see 14.2. For representative spectra of chemical finishes, see 14.3.

7.2 Both grating instruments and Fourier transform interferometers are capable of producing high quality spectra for identification and reference purposes. Other spectroscopic techniques such as laser-Raman spectroscopy, NMR spectroscopy and UV-visible spectroscopy may also be utilized, if available, to further identify the extracts. Figs. 1-5 represent infrared spectra run on an FTIR spectrophotometer with MCT detector at a resolution of 4 wavenumbers, signal averaged over 30 scans with HAPP-Gensel apodization cast on KRS-5 crystal. Fig. 6 represents a proton NMR spectrum of dimethyloldihydroxyethyleneurea (DMDHEU) cellulose reactant in deuterium oxide. Figs. 7 and 8 represent laser-Raman spectra of aqueous solutions of cellulose reactants using an argon ion laser source. Figs. 9 and 10 represent HPLC runs of cellulose reactants using Refractive Index (R.I.) detector, 5 micron C-18 reverse phase column, with 100% water mobile phase pumping at 1.0 mL/min. Fig. 11 represents an X-ray fluorescence spectrum taken from a scanning electron microscope image using a liquid nitrogen cooled detector with an energy range of 0-5 kiloelectron-volts. For other examples of infrared spectra, see 14.3 and 14.4.

7.3 Infrared Sample Preparation.

7.3.1 Techniques. Finish samples can be prepared for infrared analysis by one of the following methods: dissolve the extract in suitable solvent, for analysis as a liquid or as a cast film; grind the textile sample to small particle size and mull in mineral oil; pelletize the extract or ground textile sample into a homogeneous mixture with potassium bromide (KBr) (see 14.2).

7.4 Infrared Analysis.

7.4.1 Obtain a spectrum of the sample or extract prepared by one of the above techniques. The identity of the applied finish is confirmed by comparison of the sample spectrum with known infrared spectra. For more accurate identification, the spectrum of the known compound should be obtained with the same application and extraction history as the unknown finish.

7.4.2 Softeners. Quaternary ammonium compounds, polyethylenes, polyoxyethylene glycols, polyurethanes and polyacrylates are partially soluble in trichloroethylene or 1,1,1-trichloroethane. The extract is concentrated and transferred to a clean KBr disk.

7.4.3 Durable Press Finishing Agents. Since most durable press finishing agents can be extracted with either water or hydrochloric acid, this provides an alternate method for removing finishes for infrared spectroscopy. Approximately 0.2 g fabric, cut into small squares, is refluxed for 5 min in 0.1 *N* HCl. The solution is then decanted into a 50 mL round-bottom flask with 350 mg spectral grade KBr and evaporated to dryness on a rotary evaporator while the flask is immersed in an ice-salt bath to prevent further hydrolysis. Final drying over phosphorus pentoxide produces a residue that is mixed with more KBr (in a 50 mg:300 mg ratio) and pressed into a disk. A spectrum is obtained and compared to that of known compounds, with spectra of hydrolyzates of known compounds preferable for accurate comparison.

Another method of sample preparation for identification of durable press finishes by infrared spectroscopy is to grind the fabric and pelletize it with spectral grade KBr. Differential infrared spectra relative to ground unfinished fabric are then obtained. KBr disks containing equivalent amounts of specimen in both beams of a double beam spectrophotometer compensate for the fabric bands. Computerized spectral subtraction techniques may also be used to achieve differential spectra.

7.4.4 A quick alternative for acquiring infrared spectra of finishes was described in the 1972 Intersectional Technical Paper Competition presented by AATCC Rhode Island Section (see 14.5). The method relies on the transfer of finish by

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solvent from a small rectangle of fabric placed on the surface of an ATR crystal. The solvent is evaporated leaving a thin film of finish residue. The crystal is placed in the ATR accessory holder and the spectrum recorded.

8. Direct Spectroscopic Analysis of Fabric

8.1 With certain types of accessories and spectroscopic techniques, it is possible to acquire direct spectra of both the fabric substrate and the finishing components on it. These techniques may include infrared reflectance with ATR and diffuse reflectance accessories, photoacoustic spectroscopy (PAS), laser-Raman spectra, electron spectroscopy for chemical analysis (ESCA) and near infrared reflectance spectroscopy (NIR). In many cases, computerized spectral subtraction techniques are useful in identifying small amounts of finish on fabric.

9. Chromatographic Procedures

9.1 Chromatography is a very useful method for the separation and tentative identification of some of the finishes on textile fabrics. After separation is accomplished, identification is made by chromatographic comparison to known compounds either in pure form or after being subjected to the same application and extraction history as the unknown; identification requires comparison under at least two different sets of chromatographic conditions. Alternatively, the chromatographic peak of interest may be identified spectroscopically on line or after isolation. For most analyses, Soxhlet extracted residues or their derivatives may be analyzed by GC, HPLC or TLC. Applications included in this section are simple techniques for use with basic GC or HPLC. For information on more complex and diverse instruments and methods see 14.2.

9.2 Gas Chromatography. Gas Chromatography involves the separation of a mixture of volatile substances as it is carried through a column of surfaces that interact differentially with the various components of the mixture.

9.2.1 Formaldehyde. Formaldehyde released from fabrics may be detected by GC. A fabric sample is enclosed in a vial with a defined headspace and conditioned under precise temperature and humidity. Samples of the headspace gas are injected for GC analysis. This system can also be used to determine the amount of methanol released by hydrolysis of methylated N-methylol groups found in some durable press resins. Since the FID signal from formaldehyde is not very strong, a methanizer may be placed between the column and the flame for conversion of formaldehyde to methane. Alcohols are also converted to corresponding hydrocarbons. Conditions for formaldehyde analysis are:

Column: 3 m Porapak T
Injection time: 9 s
Bath: 65°C
Needle: 150°C
Oven: 120°C
Injection port: 180°C
Detector: 480°C

A photoionization detector may also be used for increased sensitivity. For further information on this type of analysis see 14.2.

9.2.2 Softeners, Lubricants, and Emulsifiers. Solvents such as hexane or Freon 113 are used to extract softeners, lubricants and emulsifiers from fabrics. These three groups of products are commonly made from fatty acids and fatty acid esters or their derivatives. Some of these compounds can be chromatographed directly and some must be made into derivatives to be better detected by GC.

Other long chain fatty compounds are more easily analyzed after derivatization. Monocarboxylic acids are esterified, usually with methanol, and these methyl esters are analyzed as follows: Column: 45 m × 0.25 mm DEGS open tubular column. Column temperature: 180°C.

Silylation, another method of derivatization of fatty acids and fatty alcohols, forms non-polar, volatile, thermally stable ethers. These ethers form easily, and the reactions are performed in screw-capped vials. The column used for analysis is chosen according to the type of compound that was silylated. The silyl derivatives of glycerol and mono- and diglycerides for example, are chromatographed on a 1 ft OV-1 column. Quaternary ammonium salt derivatives require a 5% SE-30 column. For more detailed discussion of this application see 14.2.

Paraffin waxes, often used as softeners, lubricants, water repellents and winding lubricants are analyzed directly by GC. Instrument conditions for paraffin wax or alpha-olefin C-30+ type hydrocarbons are:

Column: 6 ft × 1/8 in. stainless steel (SS) OV-101, 5%
Column temperature: 200C-290°C at 10C/min then hold 11 min
Detector: Flame Ionization Detector (FID) at 350°C
Injection port: 350°C
Carrier: Helium
Flow: 30 mL/min

Polyols. Water extracts of fabrics may be analyzed by GC to detect ethylene and diethylene glycols. Glycols are frequently used with or in durable press resins. Instrument conditions are:

Column: 6 ft × 1/8 in. stainless steel (SS) Tenax GC, 60/80 mesh
Column temperature: 200°C
Detector: Flame Ionization Detector (FID) at 250°C
Injection port: 250°C
Carrier: Helium at 30 mL/min

Table II—Solvent Systems for Separating Dye Classes

Dye Class	System[a]
Acid	Propanol:Acetone:Water:Acetic Acid (5:5:3:1) Pyridine:Butyl Acetate:Water (9:6:5) Butanol:Ethanol:Water (2:1:1) Propanol:aqueous ammonia (28%) (1:1)
Basic	Butanol:Ethanol:Water:Acetic Acid (10:1:1:1) Benzene:Methanol (9:1)
Direct	Propanol:Acetone:Water:Acetic Acid (5:5:3:1) Butyl Acetate:Pyridine:Water (5:5:2) Butanol:Acetone:Water (5:5:3) Organic Layer of Butanol:Water:aqueous ammonia (2:1:1)
Disperse	Benzene:Acetone (9:1) Benzene:Chloroform:Acetone (5:2:1)
Plastic	Carbon Tetrachloride:Benzene (1:9)
Solvent	Carbon Tetrachloride:Benzene (1:1)
Vat	Toluene:Pyridine (6:4) Benzene:Nitrobenzene:Acetone (8:1:1) Butanol:Butyl Acetate: Nitrobenzene:Acetone (3:3:3:1) Butyl Acetate:Pyridine:Water (5:4:2) Benzene:Pyridine:Dioxane:Acetone (20:2:2:1)

[a] Ratios are volumes of solvents; e.g., to make an eluent such as propanol:acetone:water:acetic acid (5:5:3:1), five volumes of propanol, five volumes of acetone, three volumes of water, and one volume of acetic acid are mixed (see 14.2).

9.3 Thin Layer Chromatography Procedures. TLC is the separation of components of a substance by differential travel in a solvent phase over an absorbent plate and can be an analytical tool for a variety of textile extracts such as surfactants, dye carriers, resins, polyester oligomers and, more commonly, dyes. Reasons for utilizing TLC include small sample size, preliminary work for HPLC method development or two-dimensional separation. For additional information see 14.2.

9.3.1 TLC Plates. For simplicity and uniformity in TLC separations pre-coated plates can be purchased from various manufacturers. The plates may be coated with absorbents such as alumina, cellulose, octadecyl groups (C-18) bonded to silica, or silica gel. A coating of C-18 bonded to silica is suitable for resin analysis. Dual phase TLC plates with the two phases at right angles to each other may be used for separation of emulsified products such as waxes or latex.

9.3.2 Size. The sample size should be very small. Use of a microliter syringe is recommended. When analyzing the fabric extracts it may be necessary to place

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