11—
Colorimetry for Textile Applications

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I—
Introduction

Since the introduction of CIE basic colorimetry by the Commission Internationale de l'Eclairage (CIE) in 1931, it has been the universal objective to utilize objective color measurement technology, whenever possible, for a wide variety of applications from color quality monitoring to color communication. The present chapter on colorimetry for textile applications is designed to provide the appropriate background information covering the fundamental concept of color science. A review of the various types of color measuring instrumentation and their selection is given. The proper color measuring procedure for textile materials is then introduced. Having established the necessary knowledge on color measurement technology, various practical applications in the textile industry are highlighted. Emphasis also is given to the major developments in the hardware and software of the color measuring system. The impact of such developments on the practical applications is addressed while the future prospects of the role of color measuring system in the direction of large-scale integration of color production system are highlighted. Finally, extensive references are provided in this chapter for those interested in pursuing an in-depth study of colorimetry as a textile characterization method.

II—
Background

Hardly a day goes by without the need for each of us to verbally describe at least one color. Color is not only used as a descriptive term, as most people do in their dally conversation, but also serves other important functions in commerce, industry, and science. The matching of color has been used for object identification in forensic science. The intensity of color has been used for the determination of chemical concentration in the chemical industry. Color has been used for the identification of tablets Or capsules in the pharmaceutical industry. It also has been used for the assessment of the performance of photographic materials and processes. Furthermore, it also has been used to evaluate the color-rendering performance of the light sources. There are many other application areas, including textiles, food, cosmetics, coatings, plastic, metals, ceramics, paper, and the list goes on. In all these applications, it is important that an objective method be used to specify color accurately. This is analogous to the use of a micrometer to measure length, or the use of a weighing machine to measure the weight. Here, we need a color-measuring instrument to measure color.

Color communication, in the absence of objective color specification, is frequently confusing. This is because the appearance of color is subjected to influence simultaneously by at least three very different phenomena: the light source, the object, and the visual system. The Illuminating Engineering Society defines light as "visually evaluated radiant energy." Radiant energy comprises the whole gamut from cosmic rays to radio and power transmission. Without this wide electromagnetic radiation range, the human eye can only detect the visible spectrum range from about 380 nm to 780 nm. Changes in either the radiant quantity or its spectral distribution can alter the observed color. Examples of commonly used artificial lamps are incandescent lamps, fluorescent lamps, mercury halide lamps, and sodium lamps. On the other hand, daylight is the natural light for observing color. They all have different spectral power distributions. The nature of the object illuminated can modify the quantity and quality of the incident light through selective spectral absorption, transmission, reflection, and other kinds of interactions such as fluorescence. In the context of colorimetry, there are three main classes of objects: namely, the transparent object, the translucent object, and the reflecting object—each exhibiting different ways of modifying the incident light source. The final element in the perception of color is the visual system, that is, the physiological properties of the eye that detect the modified radiant energy from the object and sends signals to the brain and, finally, the psychological processes [1–3] of the brain interpreting the received signals into response, which we call color. The subject of color and colorimetry has been studied extensively and reported in the literature [4–7].

III—
CIE Colorimetry

The Commission Internationale de l'Eclairage (CIE) is an international organization that promotes the advances of science, technology, and art in the fields of light and lighting. The corresponding English name is the International Commission on Illumination. At the sixth session of the CIE, held in Geneva in 1924, it was decided to set up a study group on colorimetry. At the seventeenth session of the CIE, held in New York in 1928, a working program was proposed to reach agreements on (1) colorimetric nomenclature, (2) a standard daylight for colorimetry, and (3) the "sensation curves" of the average human observer with normal color vision. At the eighth session of the CIE, held in England in 1931, major recommendations that laid the basis for colorimetry were made.

A—

CIE Color Specification by Tristimulus Values

In 1931, the CIE established an objective method of color specification by tristimulus values [8,9]. In this method, light source is characterized by its spectral power distribution S(λ). Objects can be characterized by its spectral reflectance curves R(λ) or spectral transmittance curves T(λ). Figure 1 shows the spectral reflectance curves of several opaque colored materials. The color vision properties of the eye can be simulated by the use of the principle of trichromacy, which postulates the existence of three response functions of the human eye generating the signals sent to the brain. In this aspect, the CIE established a standard observer [9–12], which is expressed in the form of three sets of numerical data, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$, representing the color-matching response of the average normal human observer under a standard state of adaptation and viewing conditions to the indi-

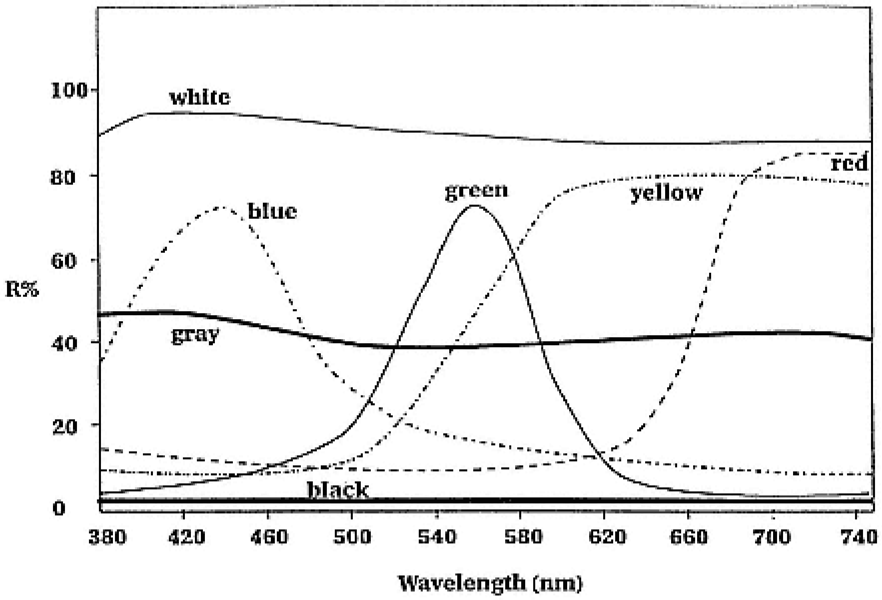


Figure 1
Spectral reflectance curves of several opaque materials.

vidual monochromatic spectrum colors. In this CIE colorimetry, three quantities called "tristimulus values" (X, Y, Z) are used to specify a color. The tristimulus values are obtained by multiplying, at each wavelength in the visible spectrum, the spectral power distribution S(λ), the spectral reflectance factor R(λ) in the case of reflecting object or the spectral transmittance T(λ) in the case of transmitting object, and the CIE standard observers $\bar{x}(\lambda)$, or $\bar{y}(\lambda)$, or $\bar{z}(\lambda)$, and then summing the products over the visible wavelength range, as shown in the following equations:

$$X = k \sum_{\lambda} S(\lambda) \cdot R(\lambda) \cdot \bar{x}(\lambda)\, d\lambda \qquad (1)$$

$$Y = k \sum_{\lambda} S(\lambda) \cdot R(\lambda) \cdot \bar{y}(\lambda)\, d\lambda \qquad (2)$$

$$Z = k \sum_{\lambda} S(\lambda) \cdot R(\lambda) \cdot \bar{z}(\lambda)\, d\lambda \qquad (3)$$

$$k = 100 / \sum_{\lambda} S(\lambda) \cdot \bar{y}(\lambda)\, d\lambda \qquad (4)$$

where k is a normalizing factor, so that for a perfect white sample it has a tristimulus Y value of 100.

In the presence of numerous kinds of light sources, the CIE also has recommended sources with defined spectral power distributions called standard illuminants [9]. They are illuminant A, which simulates the incandescent lamp, and illuminants D, representing a range of the phases of daylight differentiated by correlated color temperatures. In addition, there are a variety of F-illuminants [9], which represent typical fluorescent lamps. Among these F-illuminants, illuminants F2, F7, and F11 should take priority over others when a few typical illuminants are to be selected. F2 is a typical cool white fluorescent lamp with a correlated color temperature of 4230 K and a CIE color rendering index of 64. F7 is a broad-band fluorescent lamp with a correlated color temperature of 6500 K and a CIE color rendering index of 90. F11 is a fluorescent lamp with three narrow bands, a correlated color temperature of 4000 K, and a CIE color rendering index of 83. Under the CIE system of colorimetry, the tristimulus values for an object would change if the spectral power distribution of the incident light source changes. Furthermore, two objects would be considered a match in color under a specified condition if they have the same tristimulus values. It is possible that such a pair of objects match under one kind of source but mismatch under another source of different spectral power distribution. This kind of match is known as metameric match. On the other hand, a pair of objects would match under any light source if they have the same spectral reflectance factors. This kind of match is called nonmetameric. CIE has recommended a Special Metamerism Index: Change in Illuminant, which provides a measure of the color difference between two metameric objects caused by substituting a test illuminant of different relative spectral composition for the reference illuminant [9].

B—
CIE 1976 (L^* a^* b^*) Color Space

Subjectively, three variables commonly used to describe a color are hue, lightness, and chroma. Hue is the attribute corresponding to whether the object is red, orange, yellow, green, blue, or violet. Chroma is the attribute of a visual sensation as to the proportion of pure chromatic color. The lower the chroma of the color, the closer the color to neutral appearance. Thus a pastel tint has a low chroma, while a pure color is said to have high chroma. Lightness is the attribute of visual sensation associated with the luminous intensity of the object. Lightness can range from black to white for reflecting object and from black to perfectly clear and colorless for transparent object. The observed color difference for a pair of colors, therefore, constitutes the variations in hue, lightness, and chroma. Figure 2 illustrates the relationship of the color variables in a three-dimensional color space. Objectively, the CIE system of colorimetry also provides methods [9] for specifying the color difference between a pair of objects. The CIE 1976 (L^* a^* b^*) Color Space [13] is a popular CIE color space to quantitatively interpret the differences of two colors in a three-dimensional color space using the L^* axis, a^* axis, and b^* axis as illustrated in Figure 3. The alternate name for CIE 1976 (L^* a^* b^*) color space is CIELAB color space. The L^* axis runs through the center of the horizontal hue circle with 100 at the top representing white and 0 at the bottom representing black. At each horizontal plane cutting through the vertical L^* axis, the a^* axis crosses with the b^* axis at the center where the L^* axis runs through vertically. The a^* axis shows red when positive (+) and green when negative (-). Sim-

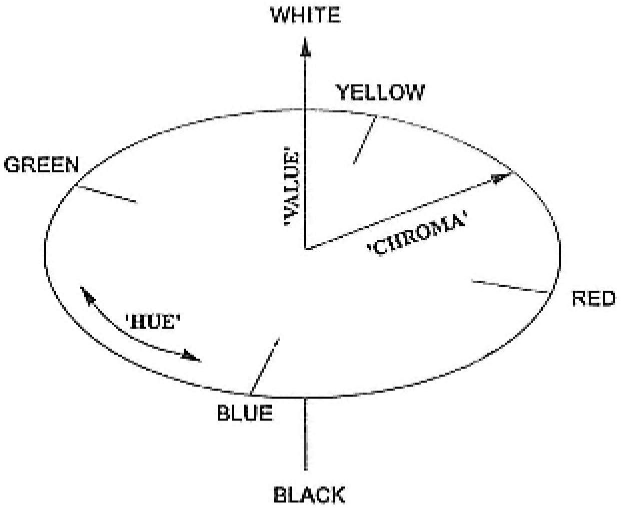
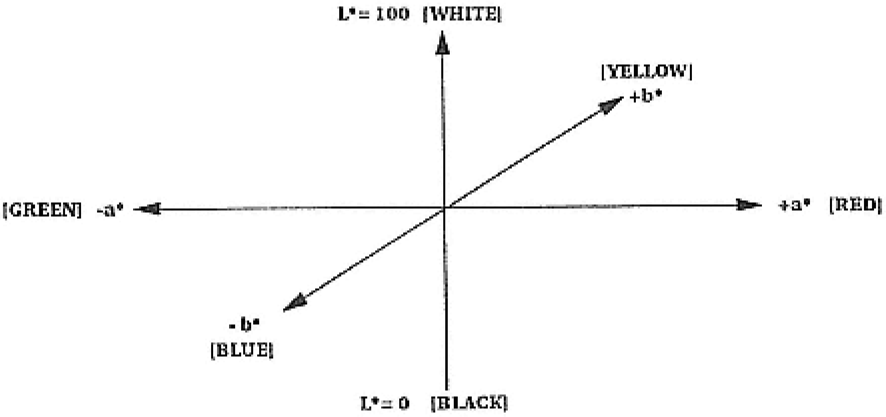
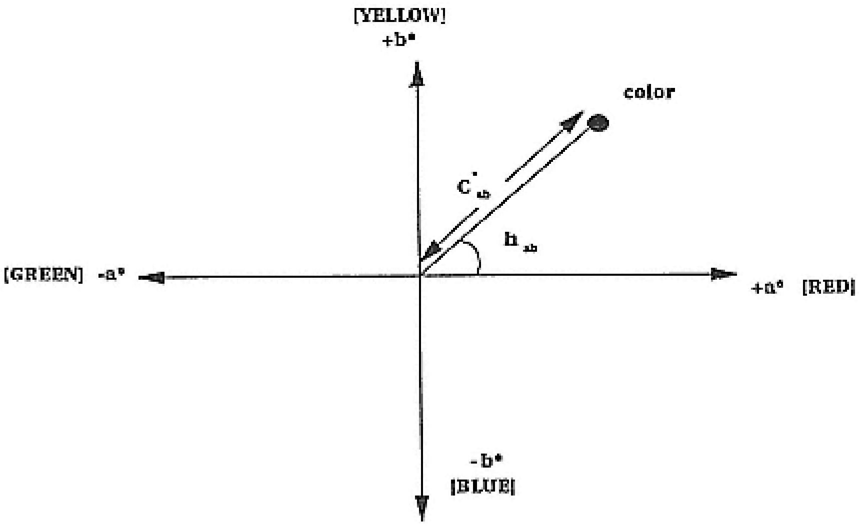


Figure 2
Relationship of hue, value, and chroma
in three-dimensional space.



(a) 3 D CIELAB Color Space



(b) a*b* Chromaticity Diagram
(Horizontal X-section of CIELAB Color Space)

Figure 3
CIE 1976 (L^* a^* b^*) color space.

ilarly, the b^* axis shows yellow when positive and blue when negative. Neutral color is indicated by a^* and b^* values being close or equal to zero. The chroma of the color increases, though not linearly, as the values, of a^* or b^* increase. The terms L^*, a^*, and b^* are defined in the following equations.

$$L^* = 116(Y/Y_n)^{1/3} - 16 \quad \text{if} \quad Y/Y_n > 0.008856 \tag{5}$$

or

$$L^* = 903.3(Y/Y_n)^{1/3} \quad \text{if} \quad Y/Y_n \leq 0.008856 \tag{6}$$

$$a^* = 500[f(X/X_n) - f(Y/Y_n)] \tag{7}$$

$$b^* = 200[f(Y/Y_n) - f(Z/Z_n)] \tag{8}$$

where

$$f(X/X_n) = 7.787(X/X_n) + 16/116 \quad \text{if} \quad X/X_n \leq 0.008856$$

or

$$f(X/X_n) = (X/X_n)^{1/3} \quad \text{if} \quad X/X_n > 0.008856$$

$$f(Y/Y_n) = 7.787(Y/Y_n) + 16/116 \quad \text{if} \quad Y/Y_n \leq 0.008856$$

or

$$f(Y/Y_n) = (Y/Y_n)^{1/3} \quad \text{if} \quad Y/Y_n > 0.008856$$

$$f(Z/Z_n) = 7.787(Z/Z_n) + 16/116 \quad \text{if} \quad Z/Z_n \leq 0.008856$$

or

$$f(Z/Z_n) = (Z/Z_n)^{1/3} \quad \text{if} \quad Z/Z_n > 0.008856$$

For these equations, X_n, Y_n, and Z_n are the tristimulus values of the illuminant.

Thus the difference in L^*, a^*, and b^* values between the reference color and the sample color may be interpreted in the following manner. Here, the convention is to subtract the reference values from the sample values.

$+\Delta L^*$: Sample color is lighter than the reference color
$-\Delta L^*$: Sample color is darker than the reference color
$+\Delta a^*$: Sample color is redder (or less green) than the reference color
$-\Delta a^*$: Sample color is greener (or less red) than the reference color
$+\Delta b^*$: Sample color is yellower (or less blue) than the reference color
$-\Delta b^*$: Sample color is bluer (or less yellow) than the reference color

The total color difference (ΔE_{ab}^*) between two colors is computed as the Euclidcan distance between the points representing them in the CIELAB space:

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{9}$$

On the other hand, when it is desired to express specifications in terms of the approximate correlates of lightness, chroma, and hue, the terms CIE 1976 lightness (L^*), CIE 1976 a,b chroma (C^*_{ab}), and CIE 1976 a,b hue-angle (h_{ab}) should be used.

The CIE 1976 a,b chroma (C^*_{ab}) provides a direct correlate of the concept of chroma and is defined by the following equation.

$$C^*_{ab} = (a^{*2} + b^{*2})^{1/2} \qquad (10)$$

The CIE 1976 a,b hue-angle (h_{ab}) correlates the concept of hue. The 0° starting point is assigned to the horizontal $+a^*$ axis. The hue-angle increases counter-clockwise around the central vertical axis of the L^* on the a^*, b^* diagram with 90° being $+b^*$ (yellow), 180° being $-a^*$ (green), and 270° being $-b^*$ (blue), and then 360° back to the $+b^*$ (red) axis again. This is illustrated in Figure 3, and the hue-angle is defined by the following equation:

$$h_{ab} = \arctan(b^*/a^*) \qquad (11)$$

Similarly, when it is desired to identify the components of color differences in terms of approximate correlates of lightness difference, chroma difference, and hue difference, the following terms should be used: CIE 1976 lightness difference (ΔL^*), CIE 1976 chroma difference (ΔC^*_{ab}), and CIE 1976 a,b hue difference (ΔH^*_{ab}).

The ΔL^* has been defined earlier, and $\Delta C_{ab}{}^*$ is the difference in $C_{ab}{}^*$ values between the two colors. The $\Delta H_{ab}{}^*$ are defined by the following equation:

$$\Delta H^*_{ab} = [(\Delta E^*_{ab})^2 - (\Delta L^*)^2 - (\Delta C^*_{ab})^2]^{1/2} \qquad (12)$$

In 1991, R. Seve [14] derived the following alternative formula for computing $\Delta H_{ab}{}^*$:

$$\Delta H^*_{ab} = 2(C_1{}^* C_2{}^*)^{1/2} \sin[(h_1 - h_2)/2] \qquad (13)$$

where subscripts 1 and 2 refer to color 1 and color 2.

Equation (13) is an improvement over Eq. (12) in that the quantity $\Delta H_{ab}{}^*$ is directly obtained with the same sign as the quantity ($h_1 - h_2$) for convenient interpretation of color difference. Hence, a pair of colors that are colorimetrically matched has a calculated value of zero for the total color difference (ΔE^*_{ab}). This quantity increases as the mismatch increases. The splitting of the total color difference (i.e., ΔL^*, Δa^*, Δb^* or ΔL^*, ΔC^*_{ab}, ΔH^*_{ab}) also has been used for color quality monitoring of a coloration process [15]. For example, the color acceptability tolerance specifications may be expressed as $\pm\Delta L^*$, $\pm\Delta a^*$, $\pm\Delta b^*$ that may vary from one location to the other location in the CIELAB space. Such tolerance volume in the CIELAB space is therefore rectangular box shaped, which is not compatible to the many research results showing the tolerance volume being ellipsoidal. An alternative color space, 1976 $L^* u^* v^*$ (CIELUV), also was recommended in 1976 by CIE [9] but is preferred by those who work in the additive color mixing industry such as the color television manufacturers.

C—
Advances in Color Difference Formulas

The CIELAB color difference formula has the limitation of being nonuniform color space; that is, equal distances in the CIELAB space do not represent equal visual color differences. Since 1976, many attempts have been made to improve this limitation [16–18] and have resulted in the following color difference formulas.

- JPC 79 formula [16]: This formula has been developed under the leadership of R. McDonald at J & P Coats, England.

- Datacolor formula: This formula has been developed under the leadership of E. Rohner of Datacolor AG (now Datacolor International), Switzerland. This color difference formula is proprietary and has not been published.

- M&S 89 formula: This formula has been developed by Marks & Spencer in collaboration with Instrumental Color Systems (now Datacolor International), England. This color difference formula is proprietary and has not been published.

- CMC (1:c) formula [17]: This formula has been developed by the Color Measurement Committee of the Society of Dyers and Colourists in England. It is an improvement of the JPC 79 formula.

- BFD (1:c) formula [19]: This formula has been developed under the leadership of B. Rigg and M. R. Luo at the University of Bradford, England.

- Berns and co-workers developed a new experimental data set that sampled color location and color difference direction to determine the mean color difference tolerance and the color difference variability of a population sample. These new results were used to fit simple empirical structures added to the CIELAB model [20].

- A team of researchers at Granada University has developed piecewise empirical models for differing areas of the chromaticity diagram to predict the coefficients of an ellipsoid formula [21].

Of these formulas, the CMC color difference formula has been adopted as the test method of the Society of Dyers and Colourists (United Kingdom) in 1984, the British Standard BS6923: 1988, and the American Association of Textile Chemists and Colorists Test Method 173–1989. In 1995, it has become an official standard of the International Standards Organization (ISO). The CMC color difference formula is an achievement of the Color Measurement Committee of the Society of Dyers and Colourists in the United Kingdom, and the Committee's initials have been adopted as the name of the formula. The CMC formula is widely used in the textile and apparel industries. The CMC color difference formula is given in the following equations:

$$\Delta E_{CMC(l,c)} = \{[\Delta L^*/(\ell \cdot S_L)] + [\Delta C^*_{ab}/(c \cdot S_c)]^2 + [\Delta H^*_{ab}/(S_H)]^2\}^{1/2} \qquad (14)$$

where ΔL^* ΔC^*_{ab}, and ΔH^*_{ab} have been defined by the CIELAB formula, and

$$S_L = 0.040975\, L_s^* / (1 + 0.01765\, L_s^*) \quad \text{if} \quad L_s^* \geq 16 \qquad (15)$$

or

$$S_L = 0.511 \quad \text{if} \quad L_s^* < 16 \qquad (16)$$

$$S_C = [0.0638\, C^*_{ab,r}/(1 + 0.0131\, C^*_{ab,r})] + 0.638 \qquad (17)$$

where subscript r of $C^*_{ab,r}$ refers to the Reference Specimen value

$$S_H = (FT + 1 - F)S_C \qquad (18)$$

where

$$F = \{ (C^*_{ab,r})^4 / [(C^*_{ab,r})^4 + 1900] \}^{1/2} \qquad (19)$$

$$T = 0.36 + |0.4 \cdot \cos(35 + h_{ab})| \quad \text{if} \quad h_{ab} \geq 345° \quad \text{or} \quad \leq 164° \qquad (20)$$

$$T = 0.56 + 0.2 \cos(168 + h_{ab}) \quad \text{if} \quad h_{ab} 164° \quad \text{or} \quad < 345° \qquad (21)$$

and where ℓ and c are relative tolerances for lightness and chroma differences, respectively, and the value of c should always remain at 1.0. It has been demonstrated that changes in hue are generally much less tolerated than changes in lightness or chroma. Thus, the ℓ and c factors may be modified to place different emphasis on lightness and chroma, respectively, in relation to hue. The values of ℓ and c are generally set to 2.0 and 1.0 for acceptability application. Other values of ℓ may be required in cases where the surface characteristics dramatically differ from flat textiles.

The CMC formula has an autotolerancing feature that can define a reasonable volume of acceptance in terms of the S_L, S_c, and S_H values, based on the location of the standard color in the CIELAB space.

D—
CIE TC1-29, Industrial Color-Difference Evaluation

In 1993, the CIE Technical Committee on Industrial Color-Difference Evaluation published a full draft of Recommendation on Industrial Color-Difference Evaluation [22]. In this draft, it recommended an extension of the CIE L^* a^* b^* uniform color space and color-difference equations for industrial color-difference evaluation with added corrections for variation in perceived color difference resulting from variation in chroma level of the color standard. A set of base conditions is defined under which the recommended model is expected to perform well. The base conditions are defined by the illumination type, illuminance, observer, background field, viewing mode, sample size, sample separation, color difference magnitude, and sample structure. When conditions of use deviate significantly from the base conditions, the introduction of parametric factors may be used to correct for the effects of experimental or material variables. The complete color-difference model for industrial color-difference evaluation is termed the CIE 1994 (ΔL^* ΔC^*_{ab} ΔH^*_{ab}) color-difference model with tye symbol, ΔE^*_{94}, and abbreviation CIE94. This formula is defined as follows:

$$\Delta E^*_{94} = \{[\Delta L^*/(K_L S_L)]^2 + [\Delta C^*_{ab}/(K_C S_C)]^2 + [\Delta H^*_{ab}/(K_H S_H)]^2\}^{1/2} \qquad (22)$$

The total color difference ΔE^*_{94} , is the distance between two color samples in lightness, chroma, and hue differences, ΔL^* ΔC^*_{ab}, ΔH^*_{ab} , weighted by weighting functions S_L, S_C, and S_H, and parametric factors K_L, K_C, and K_H.

The weighting functions S_L, S_C, and S_H adjust the total color-difference equation to account for variation in perceived color-difference magnitude with variation in the color standard location in CIELAB space. The current best estimates of these weighting functions obtained by fitting with two visual color-difference perception data sets [19,20] are defined by the following formulas:

$$S_L = 1 \qquad (23)$$

$$S_C = 1 + 0.045 C_{ab}^* \qquad (24)$$

$$S_H = 1 + 0.015 C_{ab}^* \qquad (25)$$

The parametric factors K_L, K_C, and K_H are correction terms for variation in perceived color-difference component sensitivity with variation in experimental conditions. Under the base conditions the parametric factors have assigned values of unity and have no effect on the total color difference. In the textile industry it is common to set the lightness parametric factor, K_L, to 2 while K_C and K_H are set to 1.0. The TCI-29 formulas retain the fundamental features of the CMC formula but modify the weighting functions, S_L, S_C, and S_H, based on the research results obtained by Berns and co-workers [20].

1—
Reference Documents

- Publication CIE No. 15.2 (TC-1.3) Colorimetry, 2nd Edition, Wien 3. Bezirk, Kegelgasse 27/1, Austria, 1986.

- Publication CIE No. 17 (E-1.1) International Lighting Vocabulary, Wien 3. Bezirk, Kegelgasse 27/1, Austria.

- American Standard Test Method E308-95 for Computing the Colors of Objects by Using the CIE System, ASTM, 1916 Race St., Philadelphia, PA 19103, 1995.

- AATCC 173, *CMC: Calculation of Small Color Differences for Acceptability*, Technical Manual of the American Association of Textile Chemists and Colorists, AATCC, Research Triangle Park, NC 27709.

- CIE TC1-29 Industrial Color-difference Evaluation, Full Draft No. 2: Recommendation on Industrial Color-difference Evaluation, CIE, Wien 3. Bezirk, Kegelgasse 27/1, Austria, 1993.

IV—
Color Measuring Systems

Color measuring equipment is generally classified into spectrophotometer type and tristimulus colorimeter type. The former measures the spectral reflectance factors (and spectral transmittance for Some equipments), while the latter measures the CIE tristimulus data directly.

A—
Spectrophotometers

Fundamentally, the spectrophotometer is used to compare the radiant power leaving the object with that of a reference standard at each wavelength. The instrument itself consists of a light source whose emitted light is incident onto the objects and the reflected light is then passed into the monochromator. The monochromator disperses the incoming radiant energy spectrally and transmits it via a narrow band of wavelengths through the exit slit. The detector system receives the spectral radiant power reflected from the object and the standard in close succession and generates a ratio signal that is transmitted to the computer for analysis and display. The computer is interfaced with various components of the spectrophotometer and controls its operation. With the fundamental data of reflectance factors or transmittance, one can compute all kinds of useful colorimetric data for various kinds of practical applications. Figure 4 shows a simplified diagram of a spectrophotometer.

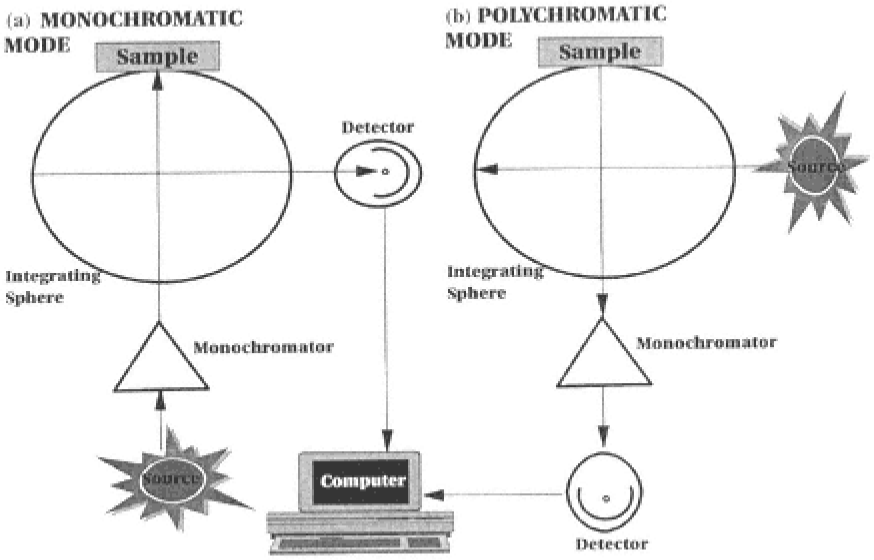


Figure 4
Simplied optical diagram of a spectrophotometer.

1—
Reference Documents

- American Standard Test Method E1331 for Reflectance Factor and Color by Spectrophotometry Using Hemispherical Geometry, ASTM, 1916 Race St., Philadelphia, PA 19103.

- American Standard Test Method E1349 for Reflectance Factor and Color Using Bidirectional Geometry, ASTM, 1916 Race St., Philadelphia, PA 19103.

B—
Tristimulus Colorimeter

A tristimulus colorimeter is an instrument with spectral response functions directly proportional to that of the CIE standard colorimetric observers. In this instrument, radiant power from the light source is incident onto the object. The reflected radiant power passes through one of the three tristimulus filters and falls onto the photodetector, causing it to give a response proportional to the corresponding tristimulus value of the object—source combination. These raw data are then transferred to a microprocessor for the computation of the absolute CIE tristimulus values. It is a useful tool for color quality monitoring of the production of a colored object. Most commercial tristimulus colorimeters are satisfactorily precise but may not agree with the tristimulus value obtained by spectrophotometry. However, there are many practical applications for which less accurate but precise instruments can still be useful, such as color quality monitoring. The tristimulus colorimeter is easy and quick to operate and is usually much cheaper than the spectrophotometric system. Figure 5 shows a simplified diagram of a tristimulus colorimeter.

1—
Reference Document

— American Standard Test Method E1331 for Color and Color Difference Measurement by Tristimulus (Filter) Colorimetry, ASTM, 1916 Race St., Philadelphia, PA 19103.

C—
Computer

At present all color measuring equipment is interfaced with computers to improve measurement speed and accuracy. A simple computer configuration includes a processor, monitor with graphic adapter, printer, magnetic disks, a suitable operating system, and the necessary application software. Additional features could include multiuser terminals and networking. The capacity of the computer ranges from microprocessor to minicomputer, depending on the application requirements. The computer serves at least four major functions.

1—
Instrument Control

The computer controls the scanning of the color measuring equipment from wavelength to wavelength with the aid of a stepping motor. It also monitors the condi-

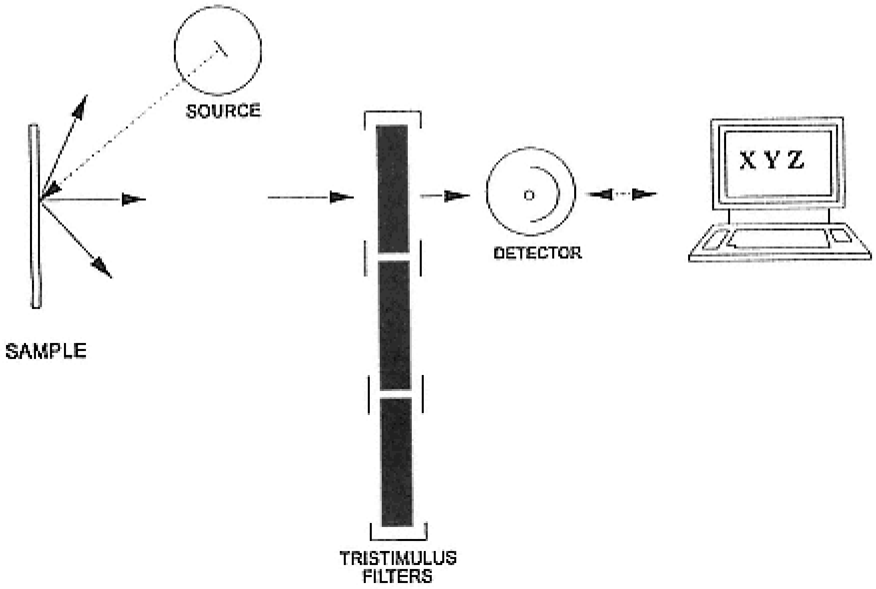


Figure 5
Tristimulus colorimeter.

tions of the equipment components such as the lamp stability. The scanning control, together with new instrument design, has improved the measurement speed dramatically in comparison with the older models.

2—

Data Transfer

The computer collects the measured data, as well as transferring the stored data for input into the specific application program for data processing.

3—

Data Storage

Many of the color measurement applications require the setup of a suitable database. Examples are the calibration information for computer color matching, acceptability data for color pass/fail, and spectral data for colorant identification. The prepared database is normally stored in the magnetic disks for later retrieval. Some users have found that the storage of the spectral data of color standards in the computer is preferred to the storage of the actual physical color standards, which may change over the storage period.

4—

Communication

Through the well-established regional or international computer network, all the useful measured information can be easily transferred to the interested party. Examples of such communications are laboratory to workshop, factory to factory, colorant supplier to users, and headquarters to overseas manufacturing plants.

D—
Selection of Color Measuring Instruments

With the advances in computer technology and the revolution in equipment design, various color measuring systems exist in the market. Different applications in different environments require different instrumentations. The following items should be considered in the selection of color measuring systems.

1. Color measuring instruments

2. Computer

3. Technical support

1—
Color Measuring Instruments

The two major types of color measuring equipments, the spectrophotometric system and the tristimulus colorimeter, measure different fundamental data. The former measures the spectral data while the latter measures the tristimulus values (usually for a specific illuminant) directly. Hence, if an application is only for color monitoring purposes with respect to color assessments for a specific illuminant, a tristimulus colorimeter is suitable. On the other hand, for computer color matching and for most colorant solution (liquid) evaluation tasks, the spectrophotometric system is a must, as the method involved requires the spectral data for implementation. In addition, a spectrophotometric system can handle all the tasks performed by a tristimulus colorimeter, although it is usually more expensive. If the system is used for color communication, then consideration should be given to whether the information would be subsequently used for colormonitoring purposes or for applications that require spectral data, such as in the case of colorant formulation.

(a)—
Spectrophotometer

In evaluating the spectrophotometer, it would be useful to examine the following features.

1. *Spectral Range*. The spectral energy distribution of the light source, the transmission characteristics of the monochromator, the intermediate optics, and the spectral responsivity of the detector should be designed for the working wavelength range. Normally, the spectral range from 400 to 700 nm with minimum data available at 10-nm intervals is practically sufficient. On the other hand, it would be preferable to have the spectral range from 380 to 780 nm with data available at 5-nm intervals in order to conform with the CIE recommendations [9]. In some special applications, the spectral range would have to be expanded up to 1100 nm for the measurement of camouflage materials for military application and down to 300 nm for colorant quantitative and qualitative analysis. Colorant analysis is usually done in solution medium, and hence the spectrophotometer should also be equipped with a transmission sample compartment, together with good resolution performance.

2. *Equipment Mode*. For color measurement, the instrument is normally set up in the polychromatic mode, such that the light source is incident onto the sample first and the reflected or transmitted light is then monochromated. If the equipment is set up in the monocromatic mode (i.e., the light source is monochromated first and the selected monochromatic light is then incident onto the sample), the measured result would be the same for the nonfluorescent sample in principle but would be incorrect for the fluorescent sample [23]. Even in the polychromatic mode, it is important that the spectral distribution of the source system should be the same as that of the CIE Standard Illuminant used for calculating the tristimulus values when measuring the fluorescent samples [23]. Some equipment types provide an option of either mode for special application such as in the evaluation of true reflectance data for the fluorescent sample for colorant formulation [24]. Figure 4 shows a simplified diagram of polychromatic and monochromatic modes.

3. *Illumination and Viewing Geometries*. The CIE has recommended four geometries defining the direction of the incident light and the direction of detecting the reflected light [9]. This can be further grouped into two major types.

In the *bidirection* type, the sample is illuminated by a beam at one angle and the reflected beam is detected at another angle such as the 45/0 or 0/45 geometries. The first number designates the illuminating incident angle while the second number designates the angle viewed by the detector. Such geometry is suitable for measuring samples that have a smooth surface, such as paint, plastic, and ink samples. In this measurement, the surface or the mirror reflection is always excluded if the sample surface is flat.

For samples with a nonsmooth surface, such as textile fabric, the so-called circumferential 45/0 (or 0/circumferential 45) geometry is preferred. Circumferential 45/0 geometry refers to the illumination of the sample at an angle of 45 degree in multiple directions around the viewing axis normal to the sample surface.

In the *sphere* type, the sample is placed at one of the port openings of a sphere, coated white internally. The sample is illuminated by diffuse light at all angles from the internal sphere wall, and the reflected light is viewed by the detector at or near the normal to the sample surface. This geometry is designated by the CIE as D/0, indicating diffuse illumination and normal viewing. Alternatively, the sample can be illuminated at or near the normal and viewed diffusely, that is, 0/D geometry. The D/0 or 0/D sphere type geometries can be used to measure samples with a relatively nonsmooth sample surface such as textile samples, with good repeatability. For flat-surface samples, the D/8 or 8/D (the number 8 designates 8 degrees from the normal) sphere type geometries provide an optional measurement of including or excluding the mirror reflection by placing a white specular component or a black trap along the 8-degree direction. Normally, for color appearance evaluation, the mirror reflection is excluded during measurement. For quantitative analysis, such as for colorant formulation application, the mirror reflection is included. Figure 6 shows the CIE recommended illuminating and viewing geometries.

4. *Other Considerations*. Other regular features have to be considered as well. These include the measurement accuracy; the measurement repeatability and reproducibility; the speed and ease of operation; the availability of special accessories such as special sample holders for powder, ultraviolet (UV), and infrared (IR) cutoff filters; and small area of view for small sample measurement. Such considerations have been reported by the Inter-Society Color Council [25].

(b)—
Tristimulus Colorimeter

As the fundamental quantifies measured by the tristimulus colorimeter are tristimulus values, the spectral range of the instrument

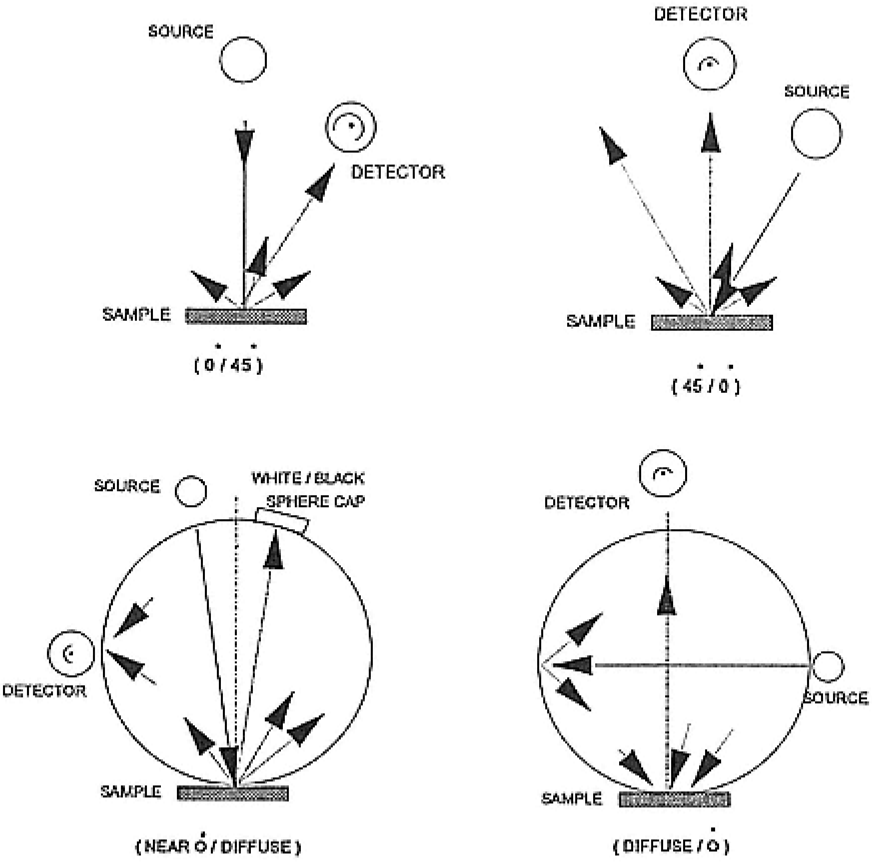


Figure 6
CIE illuminating and viewing geometries.

is limited to the visible region. It is a standard practice that the instrument is set up with the sample being illuminated directly by the light source for the reason explained earlier. Other points discussed in Section IV.D.1 should also be examined.

2—
Computer

There are basically two major types of computer systems for the color measuring equipment in the market. They are the single-user type and the multi-user type. Selection of either type depends on the present and the future requirements. The multiuser type includes a minicomputer or multiple personal computer in a networked fashion, while the single-user type is usually a personal computer. Because of strong competition in personal computer sales in conjunction with rapid advances in technology, the personal computer type color measuring system is particularly attractive and popular.

3—
Technical Support

A good color measuring system supplier should provide a quick response to users needs through the provision of a range of services. These include the installation of the system, basic and updating training programs, hardware and software maintenance, system development, and problem-solving consultancy service. In some cases, the services provided are inadequate when the place of origin of the goods is outside the users' territory. In this situation, one may need to turn to a third party for assistance, which is described in Section VII.

E—
Developments in Color Measuring Instruments

The major development for both the tristimulus type and spectrophotometric type of color measuring instruments is the reduction in physical size to a portable format with an approximate size and weight of 0.1 ft^3 and 3 1b, respectively. Such a portable format is made possible by the use of much smaller components, such as a camera-type xenon flash lamp as the illuminating source, fiber optics for light transmission, and tiny spectral filter and silicon photodiode arrays for reflected or transmitted light reception. The data processing device is also being made compact by using a microprocessor, liquid crystal display, and built-in bar-code reader. The use of these components also improves the measurement and computation speed. The portable format is attractive in measuring color objects that cannot be conveniently moved, such as of automobiles or building architecture, and for colorimetric measurements in a location not possible with a conventional tabletop color measuring instrument. In using these portable instruments at the production sites where the environment is generally hostile and dusty, the users have to be careful in measuring textile samples whose color appearance is sensitive to moisture content and heat. The relatively small sample port of the portable type instruments may affect the precision performance in measuring textile samples with enhanced surface texture. Also, major advances in terms of precision and flexibility are happening with the conventional benchtop spectrophotometer [26] as summarized in the following section

1—
Illuminating System

The instrument illuminating system is generally designed to promote precision in measuring thermochromic and fluorescent samples. The heating of the sample by the illuminating light source is minimized via the use of a sample exposure shutter or a cooler pulsed Xenon source. In addition, the fast measurement also minimizes the sample exposure time. Calibration and control of the ultraviolet (UV) content of the illuminating source is made possible by electronically controlled UV cutoff filters for accurate measurement of optically whitened textiles and to evaluate textiles colored with chromatic fluorescent dyes. In some instruments, the light source is faltered to simulate D65 illuminant to enhance the correlation of measurement results with the visual assessment of fluorescent samples under daylight illumination. The intensity of the illuminating source is also kept stable and high to enhance accurate readings of dark and saturated colors.

2—
Sample Compartment

Both the D/0 type and circumferential 45/0 type illuminating and viewing geometries remain popular for the measurement of textile samples. Some of the instrument setup can be performed automatically. This includes the selection of large area of view versus small area of view, specular component included or excluded in the case of D/0 geometry, and UV cutoff filter included or excluded. The instrument is generally equipped with a transmission compartment for transmission measurement of transparent or translucent samples, such as liquid or thin films.

3—
Monochromator System

The essential device for light dispersion has been gradually shifted from prism monochromator to the grating type monochromator. The grating version also has been switched from the ruled grating type to the holographic grating type. The holographic grating makes use of the phenomenon of light-wave interference, photographic recording, and chemical etching methods so as to rule a grating in an optical material with relatively less stray light than the mechanically ruled grating.

Another method for selectively producing narrow wavelength regions of the spectrum is the use of interference filters. This restricts the radiant energy transmitted to the relatively narrow spectral transmission band of the filter. An earlier type of such a device is discrete; that is, each filter is responsible for each narrow spectral band region and readings at intermediate wavelength regions are not available. An alternative version is the continuous variable interference wedge, whose spectral transmission varies as a continuous function of the physical location of the incident energy across the surface of the wedge. The bandwidth of the interference filter is relatively larger than that of the prism or grating type monochromator.

4—
Detector System

The detector is the light-sensitive device that registers the quantity of light being reflected or transmitted from the sample. In a single-beam instrument, the detector must remain stable between the time of detecting the light from the standard and the time for that from the sample. With a double-beam instrument the time between readings of reference and sample beams is reduced to fractions of a second, and the detector must therefore have a frequency response compatible with that used in alternating between the two optical paths.

The traditional light-detecting device is mainly the photomultiplier. This has been replaced by the tiny solid-state silicon diode photodetector array, which is positioned accurately in the dispersed spectrum so that each detector responds to a specific small band of wavelengths. This has made possible the measurement of the entire spectral data simultaneously, thus increasing the measurement speed drastically. With such a design, the measurement time for the entire visible range can be reduced to less than 1 sec, as opposed to the conventional sequential type with a measurement time of about 10 sec or more. However, such a design converts the equipment to an abridged spectrophotometer. In other words, the spectral information cannot be measured continuously throughout the spectral range and the number of measured discrete spectral data depends on the number of the silicon detectors. Instruments with as many as 76 detector elements are available in order to obtain spectral data at 5-nm intervals in the visible range. The CIE recommends that the spectral data be taken at wavelength intervals as small as possible for tristimulus integration for better accuracy [9]. Generally speaking, most applications can be carried out satisfactorily with the abridged spectrophotometer. On the other hand, the unavailable spectral information can be predicted by mathematical interpolation based on the discrete spectral data. The use of silicon detectors, coupled with the suitable light source and monochromator, can also expand the spectral range to 1100 nm for the near-infrared measurement of camouflage materials.

Recently, instrument manufacturers have created a new line of color measuring spectrophotometers called compact benchtop spectrophotometers to suit those users who do not need portability but require reasonable price, precision, and reliability [27]. The term "compact" refers to the size of the instrument, somewhere between the portable size and that of the conventional benchtop instrument. These compact benchtop spectrophotometers are of interest to large users where multiple instruments are required for a variety of applications.

The development of the color measuring sensors, coupled with the revolution in computer power and versatility as well as their integration, has led to significant advances in the performance of the color measuring systems in terms of speed, accuracy and precision. The gains in system performance have had a great impact on their areas of application.

V—
Color Measuring Procedure

A proper procedure to perform the measurement of colors is important for useful, practical applications. A normal measurement procedure involves the following steps.

A—
Instrument Setup

The spectrophotometer has to be set up in the proper mode prior to color measurement, according to the instrument manufacturer's recommendations. For example, in the case of a sphere-type reflectance spectrophotometer, the possible list of parameters to be set up includes the spectral range, the polychromatic/ monochromatic mode, the specular component in/out, the sample port size, and the selection of filters as detailed in Section IV.D.1.

B—
Instrument Calibration

After the instrument has been properly set up, it has to be calibrated for its photometric scale with respect to the 100% line and the 0% line using a white standard and a black standard, respectively, in the case of reflectance spectrophotometer. In the case of the transmission spectrophotometer, a clear solution for the solution sample (or air for the color filter sample) is used to set up the 100% reference line, and the 0% reference line is normally established by blocking the illumination beam with an opaque sample. The calibration procedure establishes a set of correction factors at each wavelength and is applied to the subsequent spectral measurements to obtain absolute spectral data.

C—
Instrument Verification

The performance of the spectrophotometer in terms of precision and accuracy can be checked by the measurement of color standards with calibrated spectral data. Precision refers to how repeatable the measurements are for the same sample over a period of time, while accuracy refers to how close the measured reading of a sample is to its absolute true reading. Examples of transmitting color standards include a series of filters (2101–2105) supplied by the National Institute of Standards and Technology (NIST). In addition, a didymium filter is useful for wavelength accuracy checking. Examples of reflective color standards include a set of 12 ceramic color files supplied by the British Ceramic Research Association. These standards may also be used to check the instrument precision (i.e., repeatability) by comparing the repeat measurements on a short-term or long-term basis. However, some of the standards are temperature sensitive and hence both the room and the sample temperature have to be conditioned to a standard temperature prior to testing.

D—

Sample Preparation and Measurement

The importance of the sample itself in providing reliable color measurement data should not be overlooked. There are a number of factors that may affect the measurement precision and accuracy. The following outlines the major items to be observed during the measurement of textile samples.

1—

Sample Temperature and Moisture Content

The temperature and moisture content of a textile sample could change its color appearance significantly and hence its measurements. It is therefore important to condition all textile samples in a room or chamber with controlled humidity and temperature for a suitable period prior to color measurement.

2—

Sample Format

A good technique of sample presentation for measurement is to ensure an identical format of presenting all the samples to be intercompared at the instrument sample port for color measurement.

(a) *Sample Opacity*. The textile fabric is usually folded to complete opacity to avoid background influence during color measurement. Thus it is important that all samples to be intercompared be folded to the same number of layers. If the measurement of the sample backed with a white background is equivalent to the measurement of the same sample backed with a black background, the sample thickness has reached complete opacity. Yarn samples should be wound onto a rigid card uniformly with identical layers. Loose fibers should be placed into a transparent cup holder with identical thickness under identical pressure. The transparent bottom of the cup holder is then presented to the sample port of the instrument for color measurement.

(b) *Sample Planarity*. Color measuring instruments are generally designed for measurement of flat samples to be placed at the sample port. If the sample extends inside the port or is displaced away from the port, different measured readings may result. If the textile sample flatness is difficult to achieve, due to surface texture, measurement behind glass will help. However, the measurement results must be corrected for effects of the cover glass, such as the Fresnel reflection.

3—

Thermochromic and Photochromic Property

Some textiles have colorants that are sensitive to heat and light. Color change on exposure to heat and light is called thermochromism and photochromism, respectively. Both the thermochromic effect and the photochromic effect can be eliminated or reduced by minimizing the time of sample exposure to the illuminating source during measurement. In addition, the thermochromism effect may be further reduced by using an illuminating source of low infrared content such as a flash xenon lamp in conjunction with an infrared cutoff filter.

4—
Fluorescence

Some textiles are colored with fluorescent colorants whose spectral emissions are sensitive to the spectral power distribution of the instrument's illuminating source system [23]. The prerequisite to measure fluorescent samples is to set up the spectrophotometer in the polychromatic mode as described in Section IV.D.1.b. The measurement repeatability of the same instrument and the measurement reproducibility of instruments of the same model depend heavily on the stability of the spectral power distribution of the illuminating source system. It is therefore desirable to measure all the fluorescent samples to be intercompared at about the same time and at the same instrument. Furthermore, the spectral power distribution of the instrument source system and the illuminating source for visual assessment should be compatible in order to obtain consistent results between instrumental and visual assessments.

In general, it is always a good practice to perform measurement averaging of multiple measurements at different locations and orientations of the test sample to achieve repeatable measurement.

5—
Reference Documents

- *Color Technology in the Textile Industry*, American Association of Textile Chemists & Colorists, P.O. Box 12215, Research Triangle Park, NC 27709. (See chapters on "The Calibration of a Spectrophotometer for Color Measurement" by Henry Hemmendinger and "Preparation and Mounting Textile Sample for Color Measurement" by R. L. Connelly.

- Society of Automotive Engineers, Warrendale, PA, Test Method J1545, "Instrumental Color Difference Measurement for Exterior Finishes, Textiles, and Colored Trim."

VI—
Textile Applications

The primary applications of color measuring systems in the textile and textile-related industries into the following four major areas: color matching, color quality monitoring, colorant solution evaluation, and color communication.

A—
Color Matching

In today's competitive world, one of the important problems of the manufacturing industry that uses color technology is how to arrive at a perfect color match with minimum of cost of dyeing and minimum time expenditure using a mixture of a few colorants. Traditionally, the procedure followed in the dyeing plant is usually a trial and error method, which gives a metameric match. During the process, one must be aware of the performance, cost, and availability of the particular colorant. The greatest drawback of this method is that no colorimetric record is kept in the trials and it takes considerable time for these trials. The method also depends on the experience of the color matcher. There is no measurement of color at any stage, and only visual assessment is done.

Computer color matching (CCM) can reduce the cost of production by:

1. Saving time in developing shade accurately

2. Providing a large number of alternative combinations of dyes for achieving the colorant formulas matching the target

3. Choosing the colorant formula for a specific requirement, such as minimum cost or minimum metamerism

4. Integration with complementary production systems for accurate and efficient data communication

5. Other associated applications, such as checking on the strength of the incoming dyes, or formulation with waste colorants

The basis of CCM is largely built upon the theory postulated by Kubelka and Munk [28] in 1931. The theory describes the scattering and absorption of radiant energy in a turbid medium in terms of reflectance, defining the quantities of radiant energy absorption and scattering by the coefficients K and S, respectively. Equation (26) defines the relationship between the reflectance factor and the Kubelka-Munk coefficients at a certain wavelength in its simplified form.

$$K/S\,(\lambda) = [1 - R\,(\lambda)]^2/2R\,(\lambda) \qquad (26)$$

The quantity K/S is related more or less linearly to the concentration of the colorant in the substrate medium and is therefore very useful in predicting the colorant formulations in conjunction with the CIE colorimetric system, to match a given color standard [29].

Although the fundamental concept of match prediction was laid down in the early 1930s, the first commercial computer color matching device was not available until 1958. This was the colorant mixture computer (COMIC), developed by Davidson and Hemmindinger [30]. It did not gain extensive popularity, largely because of its speed and flexibility, as the computer was an analog version. In the 1960s, digital computers became available, and most leading colorant makers installed their own systems of CCM to service their customers. These systems included the instrumental match prediction (IMP) system of the Imperial Chemical Industry [31] in 1963, the computer color matching (CCM) system of American Cyanamid [32, 33] in 1963, the automatic recipe formulation and optimalization (ARFO) system of Sandoz in 1964, the programmed match prediction technique (PROMPT) of Du Pont in 1965, and the computer color matching system of Ciba-

Geigy [34]. However, these systems usually had the disadvantage of poor accuracy, as the fundamental colorant calibration data were not made by the user, and the colorant formulations generated were restricted to one colorant maker. Furthermore, degree of metamerism was not indicated for certain systems. In the late 1960s, time-sharing CCM systems became available in which users could develop their own databanks. These included the systems developed by General Electric, IBM, Beckman Instruments, and the Applied Color System. So far, all these CCM systems were abridged; that is, data measured on the color measuring equipment cannot be transferred to the computer directly. In the late 1970s, CCM and other practical color measurement applications gained wide popularity because of the availability of relatively low-cost mini-computers, which are interfaced directly to the color measuring equipment. At this time, many users can afford to have such an integrated in-house CCM system with improved speed and accuracy.

In the early 1980s, CCM reached a new stage with the introduction of IBM or IBM-compatible personal computer (PC). The interfacing of the color measuring sensor with the PC meant a significant decrease in the cost of the CCM system such that the CCM system was no longer a privilege of medium-sized to large dyehouses but could also be afforded by smaller dyehouses, especially in developing countries, or for those companies that have already owned PC. Because of the open architecture of the personal computer and the affordable price, the system has become more versatile, and there are thousands of third-party softwares and accessories prepared for all kinds of applications in virtually any aspect. At the same time, the CCM system has become much more compact in size. On the other hand, the drawbacks of such systems are the much smaller central processing unit (CPU) memory and storage capacity, much slower speed, and the poorer performance in a network environment in comparison with the minicomputer version. This has rendered the PC-type CCM system more or less a personal or stand-alone system in the 1980s, whereas the minicomputer type is the multi-workstation system with a much stronger performance in network environment.

In the 1990s, the advances in information technology has greatly enhanced the performance of PC in terms of speed, memory capacity, storage capacity, and connectivity, as well as the PC network. The use of PC has dominated most color measuring system applications.

As the computer technology advanced, innovations in commercial CCM software occurred. The most evident of these is that the software is now written in a much more user-friendly manner, usually in a menu- or window-driven format with plenty of help messages and colorful graphic interpretations that were not available in the 1970s and early 1980s. Other innovations are:

1. Storage and retrieval of color standards along with relevant useful formula and process information.

2. Input of standards can be achieved by a variety of means including measurement, manual input, and electronic data transfer.

3. Assignment of performance factors for individual dyes and substrate for the correction of strength and exhaustion variation.

4. Creation of suitable dyeing groups of compatible dyestuff, substrate, and dyeing process for formulation.

5. Varieties of graphical presentations and simulated color images for assessment of the measured calibration dyeings and the predicted or corrected formulas.

6. Automatic queued match predictions of combinations of variable numbers of dyes per formula based on the preassigned standards, dye candidates, and tolerances.

7. Manual formulation or correction with support of graphical presentations.

8. Formulation for the use of surplus dyes or materials.

9. Correction can be achieved by using original dyes or new dyes or their combinations.

10. Special color matching program, such as for blending of various colored fibers for matching.

In fact, the use of CCM is so popular that such services are available at the store level in some countries. In the United States, you can walk into a paint store with a color standard requesting the store to prepare cans of paint to match the standard. Within a reasonable waiting period, a formulation based on the measurement of the color standard is predicted and the necessary amounts of the paint ingredients are automatically dispensed.

Although the technique of CCM has been practiced over 30 years, there are still a number of limitations [35], with the major ones being the poor accuracy of CCM for fiber-blends coloration [36] and for coloration with fluorescent colorants [37, 38]. However, Gibson [39] reported that the use of a neural network approach for colorant formulation shows positive results with fluorescent dyes.

B—
Color Quality Monitoring

1—
Color Pass/Fail Systems

Color pass/fail systems screen the color of the products against preset tolerances in color requirement. It is especially important in the case of large purchases. Such a preset tolerance can guarantee exactly how closely the color requirement will be met. An off shade could mean unacceptable products. Traditionally the decision as to whether a batch color is close enough to the standard being matched has been made subjectively. Due to inter- and intraobserver variability and other influential factors, subjective assessment cannot be accurate even if the observer is very experienced. The CIE system of colorimetry is normally used as a basis to carry out the color pass/fail assessment. In this system, the color difference formula is used to set the size of the tolerance for acceptability by applying lower maximum value(s) of the total color difference, chroma difference, lightness difference, hue difference as described in Section III, or any selected combinations of these variables [40–42]. In the 1990s, the use of single-color difference value for shade acceptability judgment has gained recognition in the textile industry. Reports on the performance of the use of single color difference for shade acceptability judgment have been published [43–45].

The use of color measuring systems for color quality monitoring has been extended from an offline basis to an online basis. The colored material is measured by a color measuring sensor at the production line to monitor the shade uniformity and acceptability on a real-time basis [46]. Important features of such monitoring device are the fast measurement speed, noncontact capability, good depth of focus, and large area of view. More recently, there has been development in the monitoring of color quality of textile prints by means of the colorimetric CCD camera [47].

2—
Color Sorting Systems

Color sorting systems are designed to identify the parts that can be put together in a finished product without noticeable (or unacceptable) color differences among the parts. A typical example is the application of such a system in the garment factory. Here, it is important that the various patterns that constitute the entire garment should not have noticeable color variation for a solid-shade garment. This is primarily because the various dye lots, from which the patterns are cut, have some color variations. Hence, it is necessary for the garment or dyeing factories to carry out color sorting of the dye lots prior to the pattern cutting process.

Like the color pass/fail system, the color sorting system is built on the basis of the CIE colorimetric system. The principle is to subdivide an acceptable volume of a color space, with reference to a standard color, into individual smaller volumes in which all colors located in each of these units are compatible in color and can be merged together without any unacceptable color differences. These units are usually identified with a shade numbering system based on the relative position of the individual unit from the central unit housing the standard color in a color space. Thus the individual colors inside a basic unit would be assigned with the same shade number. A popular shape of the basic unit for the shade sorting system is rectangular. One of the popular shade numbering systems is the Simon method, known as the "555" system [48]. In this system, each color is given a three-digit numeric shade sort code. Using the CIE $L^* C^{*ab} h_{ab}$ color space as an example, the first digit is an indication of the lightness of the color as compared to the standard color. If the color is lighter than the standard this digit will be above 5, and below 5 if it is darker. If the color is more saturated than the standard color the second digit will be above 5 and below 5 if it is duller than the standard. Similarly, the third digit in the shade sort code indicates the hue variation from the standard. For example, a color having the same saturation and hue except just one step lighter than the standard color would be identified with a shade sort code of 655. The dimensions of the individual units have to be varied for different color regions of the color space, and various guidelines have been provided in the literature [40, 41, 49]. Alternative shapes of the individual units in terms of rhombic dodecahedron and truncated octahedron for improved shade sorting performance in fewer groupings have been reported by McLaren [50].

The primary disadvantage of the 555 shade sorting method is that the borderline colors occupying the corners of the rectangular block are much farther removed from the center of the block than are the borderline colors that occupy the center of the faces, which may produce anomalies in shade sorting [51]. A new shade sorting technique known as Clemson color clustering (CCC) has been devised by Aspland et al. [51] to overcome this disadvantage with less shade-sorted groups. However, CCC sorting is carried out without reference to a standard. Thus the nature of the color difference of the individual color from the standard color cannot be deduced from the CCC shade sort codes. A similar color clustering technique known as the Scotsort, designed to overcome this difficulty partially by means of a primary cluster, is reported by Wardman et al. [52]. Since these color clustering techniques do not sort the colors with reference to the standard color completely, the shade sort codes for a production lot have no relationship to the shade sort codes for another production lot even though both lots are using the same standard color for acceptability judgments. To avoid this problem, it is necessary to merge the colorimetric data of the two production lots and sort the data again.

The need for color sorting is obvious and is particularly useful to those industries whose products are made up by parts in different locations.

3—
Colorant Strength Evaluation

The relative concentration of colorant compared to that of the corresponding standard colorant is routinely assessed by the colorant manufacturer during the standardization of colorants in order to maintain a high consistent quality. It is also being used by colorant users during the quality evaluation of the new shipments in order that the performance of colorants be maintained during coloration. Determinations of relative colorant strength from reflectance measurements are usually based on the Kubelka-Munk function as defined by Eq. (26). As the function is to a large extent linearly related to the colorant concentration in a substrate, the ratio of Kubelka-Munk functions of the sample and the standard at equal prepared concentration can indicate the relative colorant strength. Standard procedures for such evaluation have been worked out by some dyestuff manufacturers [53] and the Inter-Society Color Council (ISCC) [54]. A comparative assessment of the performance of various colorant strength formulae was reported by R. Hirschler [55] at the 1992 25th anniversary conference of the International Color Association (AIC) at Princeton, NJ.

4—
Whiteness Evaluation

White is a color of freshness, purity, and cleanliness. It has been used as an indicator of qualities such as freedom from contamination. The determination of the degree of whiteness has been an interesting subject for many years. In principle, it can be measured by the amount of departure from the "perfect white" position in a three-dimensional color space. However, agreement on the "perfect white" has not been reached because of a number of problems. The major problem is that strong preference in the concept of whiteness is governed by trade, nationality, habit, and product. This problem is further enhanced by the introduction of fluorescent whitening agents, the conditions of observation, and the measurement accuracy [23]. As a result, no single formula for whiteness is universally applicable. The principles for deriving whiteness formula have been described by Ganz [56–58]. In 1981, the CIE recommended field trials of a new whiteness formula [9]. The CIE whiteness formula was adopted by the American Association of Textile Chemists and Coloristis in 1989 as AATCC Method 110–1989 [59].

(*a*) *Reference Documents*

- American Standard Test Method E313 for Indexes of Whiteness and Yellowness of Near-White, Opaque Materials, ASTM, 1916 Race St., Philadelphia,PA 19103.

- Publication CIE No. 15.2 (TC-1.3) Colorimetry, 2nd edition, Wien 3. Bezirk, Kegelgasse 27/1, Austria, 1986.

- AATCC 110–1989, *Whiteness of Textiles*, Technical Manual of the American Association of Textile Chemists and Colorists, AATCC, Research Triangle Park, NC 27709.

5—
Yellowness Evaluation

The preferential absorption of white light in the short-wavelength region (380–440 nm) by the material usually causes an appearance of yellowness. Interest has developed in determining the degree of yellowness as it is considered to be associated with soiling, scorching, and product degradation by exposure to light, atmospheric gases, and other chemicals. A number of yellowness scales have been developed over the years [60–62].

(*a*) *Reference Document*

- American Standard Test Method E313 for Indexes of Whiteness and Yellowness of Near-White, Opaque Materials, ASTM, 1916 Race St., Philadelphia, PA 19103.

6—
Metamerism Evaluation

Metamerism refers to a pair of visual stimuli that in the human eye give rise to identical colors but that have different spectral energy distribution, as described in Section III.A. Visual stimuli could be the light source entering directly into the eye or modified reflected light into the eye from the objects. In the latter case, the visual stimuli could be modified by changing the spectral power distribution of the light source. Either change causes an identical match or mismatch of the objects. This phenomenon is commonly called source metamerism. It is important to predict the degree of mismatch for a set of color-matched products when the light source changes, using a source metamerism index in computer color matching. One can select the least metameric recipe from a large number of alternative recipes generated by the system if one can evaluate the size of metamerism for each predicted recipe. The CIE has recommended a special index of metamerism for change of illuminant in 1972 [63]. Other means of computing metameric indices were assessed by Badcock [64] and Choudhury et al. [65].

a. Reference Document

- Publication CIE No. 15.2 (TC-1.3), Colorimetry, 2nd edition, Wien 3. Bezirk, Kegelgasse 27/1, Austria, 1986.

7—
Color Fastness Assessment

Most methods in color fastness assessment of textile materials involved treating the dyed material in a standardized manner and then comparing the treated textile and the original untreated textile (with respect to the color change) visually versus a gray scale that carries a series of pairs of color chips with increasing color difference magnitude. There are two kinds of gray scales, one for the "staining" test and the other for "change of shade." The obvious disadvantage of determining the color fastness rating by means of visual assessment is the poor reproducibility from observer to observer. Methods for instrumental assessment of staining and change of shade have been developed by various professional bodies. At the International Standards Organization (ISO) technical committee (TC38/SCI) meeting in Bad Soden, Germany, in 1987, a German proposal for instrumental assessment of staining was accepted [66]. At the ISO TC 38/SCI meeting in Williamsburg, VA in 1989, the Swiss proposal on instrumental assessment of change in shade was accepted [66].

(a) Reference Document

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8—
Luster Evaluation

Some textile fabrics are finished with a lustrous appearance via a calendering process. The luster is the gloss appearance associated with the contrast between the specularly reflecting area of fabric and the surrounding diffusely reflecting area [67]. Hunter has developed a formula [67] to express this relationship.

$$\text{Luster} = 100(1 - R_d/R_s) \tag{27}$$

where R_d is the diffuse reflectance factor and R_s is the specular reflectance factor.

C—
Colorant Solution Evaluation

A spectrophotometer equipped with transmission measurement may also be used to evaluate a colorant solution for a number of applications. This includes the determination of solubility and solution stability of water-soluble dyes [68, 69], the evaluation of relative colorant strength based on solution measurement [70], the monitoring of dye exhaustion characteristics [71], and the evaluation of formaldehyde content [72]. These evaluations are largely based on Beer's law, which states that the measured quantity of absorbance is directly proportional to the concentration of the absorbing species present in a solution [73]. The quantity of absorbance is equal to the logarithm of the inverse of the transmittance. This law has been very useful in various quantitative analysis and the investigation of dyeing mechanisms [74]. On the other hand, transmission measurement of colorant solution has also been used for qualitative analysis of organic pigment [75].

With increasing concern in regard to the effluent color of the textile finishing industry, quantitative techniques, based on transmission measurement, have been devised by the American Dye Manufacturers' Institute [76] in the United States and the National Rivers Authority [77] in the United Kingdom to monitor the color of wastewater effluent as an indicator of water quality.

D—
Color Communication

Various ways, with differing accuracy, have been devised to communicate color. These includes the use of general color names, the method of designating colors developed by the Inter-Society Color Council and the National Bureau of Standards [78], the use of color order systems with a systematic collections of color standards sampling the color space such as the Munsell notations [79], and the CIE system [9]. Of these methods, there is no doubt that the CIE system provides the highest precision. Furthermore, one can easily use the CIE color specifications for quick distant communication via an international telecommunication system. One drawback of the CIE color specification system is the absence of the real physical color accompanying the numeric specifications. Otherwise, it would be useful as a color development tool by designers for styling applications for example. Such a drawback has been, to some extent, overcome by the development of calibrated color display system where it is possible to generate a variety of image colors with CIE colorimetric specifications by controlling the red, blue, and green guns of the cathode ray tube in an appropriate fashion [80–85]. Calibrated color display systems have been utilized in computer-aided color manipulation (CCMAN) systems to aid color selection and visualization in the design creation process as well as for color communication with external systems. However, the success of this method requires further research due to a variety of technical and visual observation problems [81, 86]. The phenomenon of metamerism complicates the colorimetric calibration of CAD/CCMAN systems including the color monitors, scanners, and printers. The colors of the original and its reproduction at the monitors or printers are usually predicted to match only under one illuminant. In addition, color reproduction performance is further limited by the mismatch of color gamuts among the monitors, printers, and scanners. CIE Technical Committee 1–27 has published guidelines for evaluation of color appearance models for reflection print and self—luminous display image comparisons with respect to color reproduction [87].

VII—
Sources of Technical Information on Color Science

The science and technology of color have been changing and advancing rapidly. Research on various aspects is being carded out at various places. It is sometimes difficult for a beginner to locate the necessary information as well as the bodies that provide the required technical assistance. The following is an attempt to provide the sources where technical information or assistance is available.

A—
International Associations

There are two major international associations that promote the study, advancement, and exchange of information on color science. They are the International Commission on Illumination (CIE) and the International Color Association (AIC) [88]. CIE is particularly active in recommending technical standards and working procedures.

B—
National Associations

On a national basis, most countries have their own national association in developing the science and technology of color. Most national associations are also members of the AIC and CIE. Examples are the Inter-Society Color Council (United States), the Canadian Society for Color in Art, Industry and Science, the Color Group (Great Britain), the Hungarian National Color Committee (Hungary), the Color Science Association of Japan, the Hong Kong Illumination Committee, AIC-Verbindungsausschuss (ER. Germany), Centre d'Information de la Couleur (France), Associazione Ottica Italiana, and Pro Colore (Switzerland).

C—
Technical Assistance

Technical assistance on the consultation, measurement, and training programs is available from three major sources: technical institutes, educational institutes, and instrument manufacturers. The technical institutes are usually supported by the local governments. Examples are the National Institute of Standards and Technology (United States), National Physical Laboratories (United Kingdom), National Research Council (Canada), Bundesanstalt fur Materialprufung (ER. Germany), Electro-Technical Laboratory (Japan), and National Office of Measures (Hungary). Many educational institutes are particularly active in research and the provision of training programs. These include the Rochester Institute of Technology

(Unites States), Clemson University (United States), Hong Kong Polytechnic, and University of Derby (United Kingdom). Equipment manufacturers also provide technical assistance such as training programs, which are, as expected, usually product oriented. Examples of color measuring equipment manufacturers are HunterLab, Kollmorgan, BYK-Gardner, and X-Rite (all United States), and Datacolor International (Switzerland) and Minolta (Japan). On the other hand, the readers should not neglect the abundant valuable publications available in the public domain that report the latest developments in color research and application. Examples of these publications can be found in the Reference section.

VIII—
Future Prospects

Since the introduction of the CIE basic colorimetry in 1931, the developments in color measuring systems have been enormous. Substantial advancements have been achieved in both the hardware and software applications. During this growth period, other coloration-related systems have also been developed:

- Computer-aided design (CAD) system. A system to aid designers to create/ manipulate design with digital information.

- Computer-aided color manipulation (CCMAN) system. A system, complementary to the CAD system, to aid color selection and visualization in the design creation process with CIE colorimetric data for color communication with external systems. The CAD and the CCMAN systems are sometimes merged into a single system.

- Computer-aided colorant dispensing (CCD) system. A system for dispensing the required amount of the individual colorants and chemical auxiliaries into the color production system. The colorant formula is usually originated from the computer color matching (CCM) system.

- Computer-aided process control (CPC) system. A system for monitoring and controlling the process variables of the coloration process.

- Computer-aided color monitoring (CCMON) system. A system for monitoring the color quality of the color production.

To some extent, substantial integration of these systems has already been achieved in the laboratory and production environment. In the next decade, technology development will be in the direction of total integration for the purposes of improving accuracy, precision, and efficiency, as well as quick response. The color of the design obtained from CAD/CCMAN will be transmitted to the CCM, where the colorant formulations will be predicted, and the selected recipe will pass on to the CCD for dispensing the required amounts of colorants and chemicals into the production system, where the CPC with the aid of CCMON will monitor and control the entire production process. Such an integrated system can communicate with another similar system or just a CAD/CCMAN device at another location via

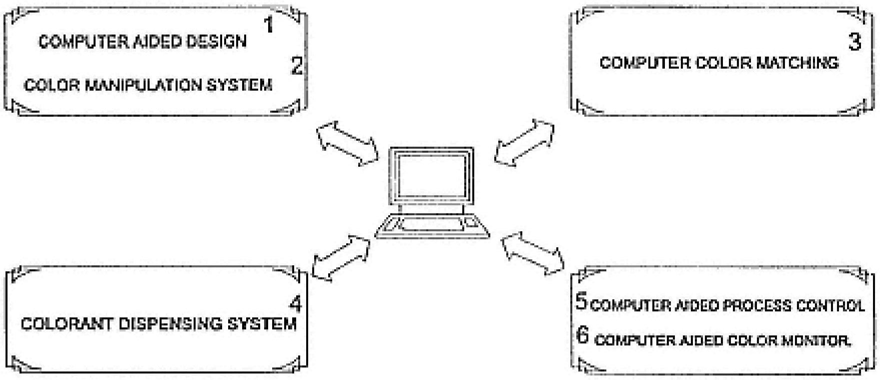

Figure 7
An integrated color production system:
(1) a system to aid product design;
(2) a system to aid color selection and manipulation with CIE colorimetric specifications for color communication;
(3) a system to assist colorant formulations;
(4) a system to dispense the required amount of each colorant into the production system;
(5) a sytem to control the operation of the production system; and
(6) a system to monitor the color quality of the product.

network. The national and international information superhighways will play a major role in linking the appropriate systems together to be used by all elements of the textile product chain to enhance productivity and competitiveness. Figure 7 shows the concept of a large-scale integrated color production system that can interface to other similar systems.

IX—
Conclusion

In less than half a century, color measuring devices have evolved from a stand-alone unit to a computer-interfaced system and are moving in the direction of total integration. At the same time, the application environment has also evolved from the research laboratory to the manufacturing and retail sectors, The target is to let the usefulness of such devices reach the general public in their daily lives. The evolution in color science has been greatly assisted by the developments in and use of computers.

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12—
Assessment of Chemical Barrier Properties

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1—
Introduction and Background

Various forms of chemical resistance testing are used to assess the barrier properties of textile materials when used in applications requiring barrier performance. In most cases, information from this testing is used to support decisions for the development, selection, and use of products that require some level of chemical resistance. One of the foremost applications of textile materials involving the need for chemical resistance is for their use in protective clothing (Fig. 1), As a consequence, many of the chemical resistance evaluation methods have evolved from the chemical protective clothing industry. An important part of this industry has been the establishment of standard test methods that ultimately guide product innovation and claims. While many test techniques have been developed specifically for evaluating protective clothing, they may easily be applied to any use of textile material where chemical resistance determinations are needed. This chapter has been written to provide an understanding of the test methods available for evaluating the chemical resistance of textile materials and is intended to help those with testing needs to correctly choose test methods and interpret test results for chemical barrier performance.

A—
Chemical Barrier Materials

Barrier performance-based products require unique materials that are capable of preventing chemicals in a particular state and concentration from passing through the materials used in their construction. For the most part, textiles by themselves are generally only able to resist solid (particulate) penetration, and sometimes liquid penetration depending on the nature of the liquid challenge and surface characteristics of the material. Most chemical barrier materials for liquids

Figure 1
materials are an integral part of
protective clothing. Shown here is a
proprietary plastic laminate on a nonwoven
substrate as part of encapsulating suit for
total protection of the wearer.
(Courtesy of Kappler, Inc.)

and gases are composed of a film or coating in combination with a substrate fabric. The film or coating may be on one side or both sides of the fabric. In general, the film or coating provides the properties of the material, while the substrate fabric mainly provides material strength and support.

Films and coatings comprise a number of materials, either elastomeric or plastic in polymer composition. Examples of elastomeric films include Neoprene (chloroprene), nitrile rubber, butyl rubber, chlorobutyl rubber, Viton (fluoropolymer), and various combinations of these polymers. Plastics and thermoplastics are increasingly being used for products owing to their relatively "good" chemical resistance. Traditionally, polyvinyl chloride, polyurethane, and polyethylene have been used. However, the diversity of these plastics is expanding as manufacturers produce a variety of laminate materials that include different polymer layers with varying levels of chemical resistance in order to provide overall chemical resistance to a broader range of chemicals, such as in Saranex and a proprietary Teflon film [1].

Another type of materials being used in products is microporous films, which are engineered with pores ranging in size from 0.01 to 10 μm. These materials generally offer "breathability" in terms of water vapor transmission and sometimes air permeability (see Fig. 2). These materials are designed to offer liquid or particulate penetration resistance, but because of their structure, they cannot provide an effective to vapor penetration by most chemicals [2].

Substrate fabrics may be of woven or nonwoven types. Nylon, polyester (Dacron), Nomex, and fiberglass fabrics are common examples of woven supporting fabrics used in chemical protective garments. Nonwoven materials include polyester, polypropylene, and spun-bonded polyethylene. The substrate fabrics are either laminated to the plastic or rubber film/sheet under heat and pressure or coated with a solution of the plastic/rubber material.

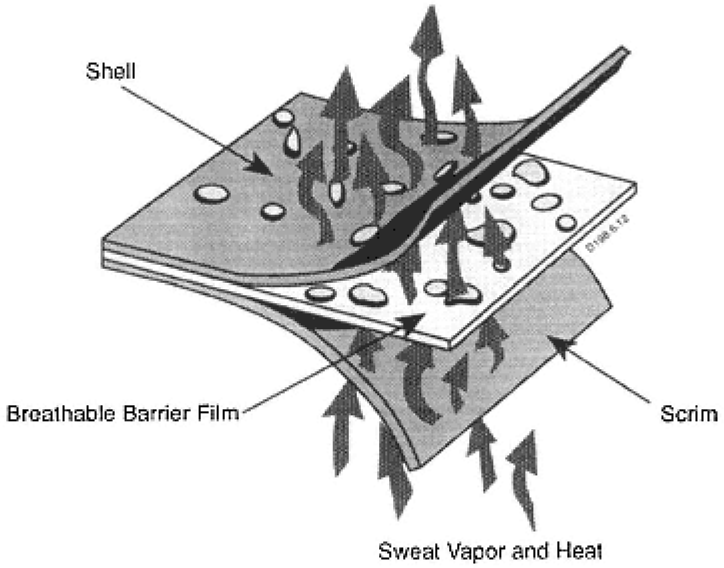

Figure 2
Some protective materials incorporate a microporous film. These materials are designed to prevent liquid penetration while allowing air and water vapor to pass through the material, providing greater comfort to the wearer.
(Courtesy of W. L. Gore & Associates.)

Textiles may also be combined with adsorbent materials that are designed to prevent the passage of aerosols or chemical vapors. These types of fabrics have been traditionally used for chemical warfare agent protection within the military, but their breathable characteristics make these types of fabrics suitable for applications where low levels of air chemical contamination may be encountered [3].

B—
Standards Pertaining to Chemical Barrier Performance

Though a number of driving forces are responsible for large changes in chemical technology, one of the primary reasons for these changes can be traced to the introduction of new testing standards. In the United States, consensus group standards established by the American Society for Testing and Materials (ASTM) and related industry trade group standards have been predominantly used for evaluation of product chemical performance. Many of these have been developed by ASTM Committee F-23 on Protective Clothing, Committee D-11 on Rubber, Committee D-13 on Textiles, and Committee D-20 on Plastics. Outside the United States, the most significant standards development groups are the European Standardization Committee (CEN), which is in the process of developing standards for the European Community, and the International Standards Organization (ISO). A list of standards relevant to this chapter, with their current edition, is provided in Appendix A of this chapter.

C—
Overview of Chemical Resistance Test Approaches

Chemical resistance test approaches for chemical textile-based products may be segregated into small-scale, material-based tests and full item evaluations. Material test approaches can be classified into three types, which describe how chemicals may interact with materials:

- Degradation resistance

- Penetration resistance

- Permeation resistance

A number of different procedures exist for the measurement of each phenomenon, depending on the type of chemical challenge and the level of sophistication for performing the tests. Of the material testing approaches, both penetration and permeation resistance testing allow assessment for the qualities of a protective clothing material, whereas degradation resistance does not. Penetration testing may involve chemical particulates, liquids, or vapors (gases). This chapter specifically addresses liquid and vapor challenges. Similarly, since various applications involve chemical materials, overall product testing is not described in this chapter.

The individual procedures available for measuring chemical degradation, penetration, and permeation resistance are described in the following sections.

II—
Degradation Resistance

Degradation is defined by ASTM's F-23 Committee as the "change in a material's physical properties as the result of chemical exposure." Physical properties may include material weight, dimensions, tensile strength, hardness, or any characteristic that relates to a material's performance when used in a particular application. As such, the test is used to determine the effects of specific chemicals on materials. In some cases chemical effects may be dramatic, showing clear incompatibility of the material with the chemical. Figure 3 shows a specimen of a protective clothing material before and after its exposure to a selected chemical, illustrating a severe case of material chemical degradation. In other cases, chemical degradation effects may be very subtle.

Various groups have examined different approaches for measuring the chemical degradation resistance of materials, but no single generalized test method has been developed by consensus organizations within the United States, Europe, or internationally [4]. Nevertheless, various techniques are commonly used for rubber and plastic materials within different material industries. These procedures and their utility in evaluating chemical materials are discussed next.

A—
Specific Testing Approaches

While not specific to any particular product, a few test methods have been developed for evaluating chemical resistance of different materials. These are:

- ASTM D471, *Test Method for Rubber Property-Effect of Liquids*
- ASTM D543, *Test Method for Resistance of Plastics to Chemical Reagents*
- ASTM D3132, *Test Method for Solubility Range of Resins and Polymers*

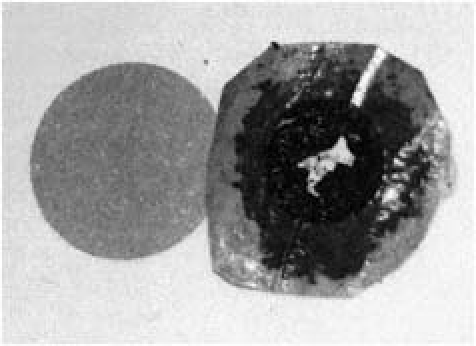

Figure 3
Plastic-coated nonwoven fabric
before (left) and after (right)
exposure to sulfur trioxide.
(Courtesy of TRI/Environmental, Inc.)

However, a few specific test methods have been developed for protective clothing:

- ASTM F1407, *Test Method for Resistance of Chemical Protective Materials to Liquid Permeation-Permeation Cup Method*. This test as developed by ASTM's F23 Committee also allows for determining chemical degradation of protective clothing materials; however, this method is primarily intended to provide a simple technique for measuring chemical permeation of protective clothing.

- ISO 2025, *Lined industrial rubber boots with general purpose oil resistance*. This test involves a footwear specification that include measuring footwear material degradation to oils.

- The National Aeronautics and Space Administration (NASA) has developed a method to determine degradation of fabrics used in propellant handlers ensembles [5].

These techniques have been grouped by the type of approach used in the following sections. Table 1 summarizes the key characteristics, differences, and applications of each approach for measuring the chemical degradation of protective clothing materials.

1—
Degradation Tests Using Immersion-Based Techniques

ASTM D471 and D543 establish standardized procedures for measuring specific properties of material specimens before and after immersion in the selected liquid(s) for a specified period of time at a particular test temperature. Test results are reported as the percentage change in the property of interest. ASTM D471 provides techniques for comparing the effect of selected chemicals on rubber or rubber-like materials, and is also intended for use with coated fabrics. ASTM

Table 1 Comparison of Chemical Degradation Test Methods

Test method	Type of contact	Contact period	Determination	Sample handling
ASTM D471	Both immersion and one-sided	22–760 hr	Weight, volume, or other physical property change	Acetone rinsing followed by blotting
ASTM D543	Immersion only	Up to 7 days	Weight, volume, or other physical property change	Solvent rinsing depending on chemical followed by blotting
ASTM D 3132	Immersion only	24 hr	Visible condition of sample	None
ASTM F1407	One-sided	Unspecified	Weight Change	Blotting
NASA MTB- 175–88	One-sided	1 hr	Weight change,visible condition of sample	Blotting

D543 covers testing of plastic materials, including cast and laminated products, and sheet materials for resistance to chemical reagents. In each test, a minimum of three specimens are used whose shape and size are dependent on the form of the material being evaluated and the tests to be performed. An appropriately sized vessel, usually glass, is used for immersing the material specimens in the selected chemical(s). Testing with volatile chemicals typically requires either replenishment of liquid or a reflux chamber above the vessel to prevent evaporation.

The two sets of procedures prescribe a variety of exposure conditions and recommended physical properties. In general, the test methods can be applied to any type of liquid chemical challenge. ASTM D471 cites a number of ASTM oils, reference fuels, service fluids, and reagent-grade water. ASTM D543 lists 50 different standard reagents, which include representative inorganic and organic chemicals. In ASTM D471, 17 different test temperatures ranging from -75°C to 250°C, and five different immersion periods (22 to 760 h) are recommended. ASTM D543 suggests a 7-day exposure at either 50 or 70°C. For determining chemical degradation resistance, ASTM D471 specifies procedures for measuring changes in mass, volume, tensile strength, elongation, and hardness of rubber material, and breaking strength, burst strength, tear strength, and coating adhesion for coated fabrics. Measurement of material specimen mass and dimensions is recommended in ASTM D543, while other properties may be selected that are appropriate for the material's application.

Both test methods indicate that the selected exposure conditions and physical properties measured should be representative of the material's use. For protective apparel material testing, this will usually mean specifying significantly shorter test durations and ambient temperature exposures. Since the methods are intended for comparing materials against similar chemical challenges, no criteria are given for determining acceptable performance.

2—
Degradation Tests Using One-Sided Exposure Techniques

Section 12 of ASTM D471 provides a procedure for evaluating the effects of chemicals when the exposure is one-sided. This technique is particularly useful for the evaluation of protective clothing materials, particularly those involving coated fabrics, laminates, and any nonhomogeneous material. In this procedure, the material specimen is clamped into a test cell (Figure 4) that allows liquid chemical contact on its normal external (outer) surface. Usually changes in mass are measured for this testing approach, since the size of the material specimens is limited.

A similar procedure was developed by the ASTM F23 committee [6] but was never established as a standard test method. This test method involved the same approach as in ASTM D471 (Section 12) but was specific to evaluation of protective clothing materials. The proposed test method used a chemical degradation test fixture that was a simple "sandwich" configuration consisting of three identical one-chamber glass pipe cells held between top and bottom polyethylene boards by a series of wing nuts. Material specimens were positioned between the bottom

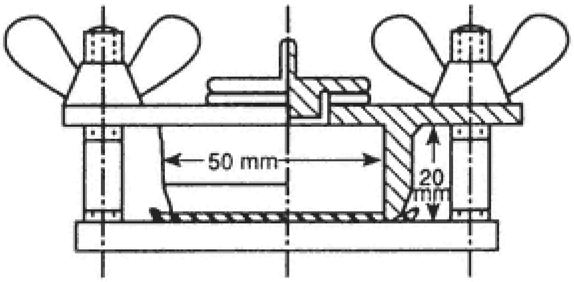

Figure 4
Degradation test cell design for
one-sided exposure
as specified in ASTM D471.

board and the glass pipe cells. Liquid chemical was then poured into the cell to initiate contact with the material specimens. Following the end of the exposure period, the material specimens were blotted dry and then evaluated for the property of interest. Mass, thickness, and elongation were originally prescribed as physical property measurements in the technique, but the committee later debated the need for evaluating material elongation since different types of substrates significantly affected the ability of the test to compare supported and unsupported materials. An interlaboratory test program for validating the technique also indicated serious problems in method reproducibility and difficulty in conducting the test when severe chemical degradation occurred.

The ASTM F23 Committee more recently developed a procedure that, while intended for measuring chemical permeation resistance, serves as a useful technique for evaluating chemical degradation resistance of protective clothing materials [7,8]. ASTM F1407 employs a lightweight test cell in which the material specimen is clamped between a Teflon-coated metal cup filled with the selected chemical and a metal ring (flange). The entire cup assembly is inverted and allowed to rest on protruding metal pins, which hold the test cell off the table surface. In the mode of permeation testing, the weight of the entire assembly is monitored; however, for use as a degradation test, the test cell serves as a convenient means for evaluating changes in material mass and thickness. Visible observations are also recorded as part of the testing protocol. Figure 5 shows a photograph of the permeation test cup specified by this method.

Each of the test methods described thus far for surface contact is provided for the testing of liquids. Protective clothing specimen chemical degradation can also be evaluated for chemical gas or vapor exposures. During one study for screening chemical resistance of protective suit [9], a special test cell was designed for evaluating material performance against gases. This cell was configured to provide a leak-free seal with the material specimen and to allow the flow of the gas into and out of the test cell. Degradation results for three protective clothing materials are shown in Table 2 for both liquids and gases.

Figure 5
Permeation test cup and field test kit conforming to ASTM F1407,
which may also be used for measuring barrier material chemical
degradation resistance.
(Courtesy of TRI/Environmental, Inc.)

NASA has developed and uses an internal procedure (MTB-175-88) for examining material responses to liquid propellants [5]. In one part of the test, 0.5 ml of the test chemical is placed on the middle of a 2-inch-square material specimen. Temperature rise of the material sample is monitored using a sheathed thermocouple, with subsequent observation of visible changes in the sample's appearance such as burning, smoking, frothing, bubbling, charting, solubilizing, fracturing, and swelling. The second part of the test involves applying a larger amount of test chemical to material specimens for the purpose of measuring changes in thickness and tensile strength.

An extension of the NASA procedure involves applying differential scanning calorimetry and thermogravimetric analysis as another means for determining material chemical degradation. Bryan and Hampton [10] examined the effects of liquid nitrogen tetroxide and monomethyl hydrazine on the breaking strength of a chlorobutyl rubber coated Nomex material. They found that the time of exposure could be determined by differential scanning calorimetry and that a correlation existed between the breaking strength of the fabric and an endothermic event occurring during the analysis of the fabric.

3—
Degradation Testing Using Solubility-Based Evaluations

Henriksen [11] first proposed the application of solubility parameter measurements in the selection of chemical protective clothing barriers. His recommenda-

Table 2 One-Sided Immersion Degradation Resistance Data for Selected Materials and Chemicals

	Viton/chlorobutyl laminate			Chlorinated polyethylene			FEP/Surlyn laminate		
Chemical	Percent weight change	Percent elongation change	Visual observation	Percent weight change	Percent elongation change	Visual observation	Percent weight change	Percent elongation change	Visual observation
Acetaldehyde	10	0		24	11		0	-5	
Acrylonitrile	9	0	Delaminated	35	Failed		-1	0	
Benzene	2	0		60	Failed		0	0	
Chloroform	4	0		72	Failed		0	0	
Dichloropropane	3	0		120	Failed		-2	0	
Ethyl acrylate	17	0	Curled	160	Failed		0	0	
Ethylene oxide	2	0		13	11		0	0	
Hydrogen fluoride	4	0	Discolored	2	11	Discolored	4	0	
Nitric acid	9	0	Discolored	8	-6		-1	0	

Note: FEP Fluorinated ethylene propylene. Percent elongation based on elongation measured using ASTM D412 for exposed and unexposed samples; "failed" results indicate materials not tested due to weight changes over 25%.
Source: Adapted from Ref. 9.

tion of use of three-dimensional solubility parameters was based on the early work of Hansen [12], who successfully demonstrated that chemical effects could be correlated with the solubility parameters of individual chemicals for resins and other homogeneous materials. Hansen postulated that the chemical's energy of evaporation, ΔE, is the sum of the energies arising from dispersion forces, ΔE_d, polar forces, ΔE_p, and hydrogen bonding forces, ΔE_h. Dividing ΔE by molar volume (V_m) gives the cohesive energy density for each solvent:

$$\delta = \left(\frac{\Delta E}{V_m}\right)^{1/2} \qquad (1)$$

The three-dimensional solubility parameter is defined as a vector of magnitude δ, with components, δ_a, δ_p, and δ_h, derived from the energies resulting from the three types of molecular forces. Thus, the solubility parameter of a given substance can be visualized as a fixed point in three-dimensional space. Hansen [13] conjectured that the closer the solubility parameters of two substances lie within the three dimensional system, the greater their affinity and similarity of response to other substances. Hansen found that a sphere could be defined in solubility parameter space for each polymer such that when exposed to solvents with solubility parameters lying within the sphere, the polymer would interact (i.e., dissolve, swell, etc.), whereas those solvents lying outside had relatively little effect. Figure 6 shows this schematically with two-dimensional projections on Cartesian planes.

Estimation of a three-dimensional solubility parameter "sphere" has become one technique to evaluate the chemical degradation resistance over a wide range of substances. Holcomb [14] advanced a technique for determining the solubility parameters of polymer substances that involved observing and measuring changes in a material when exposed to a large battery of chemicals representing ranges in each of three solubility parameter dimensions. The principle of this technique follows immersion testing where small specimens of a material are placed in each of the solvents and changes in visual appearance, mass, or volume are determined. These procedures are embodied in ASTM D3132, where a battery of solvents is used to show effects on the material by virtue of the measurements or observations that define the solubility space for the polymer. Bentz and Billing [15] and Perkins and Tippit [16] both applied this technique to a number of polymer substances. Instead of using the 90 different solvents and solvent mixtures specified in ASTM D3132, they used the smaller 55 "neat" chemicals listed in Table 3 and originally suggested by Holcomb [14].

Use of solubility parameter-based techniques for measuring the chemical degradation of protective clothing materials allows the researcher to quickly and comprehensively characterize the effects of chemicals on a given material. In essence, when a solubility sphere can be defined for the test material, the technique can be used as a predictive model to characterize performance against other solvents (those not in the test battery) without testing. Nevertheless, the method

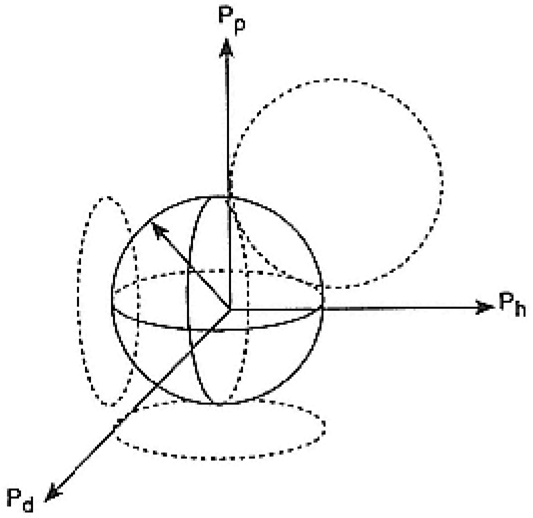

Figure 6
Hansen three-dimensional solubility plot. The sphere indicates the solubility space. The circles represent solubility areas projected by the sphere in two dimensions.
(From Ref. 16.)

Table 3 List of Chemicals Used in Degradation Tests to Determine Material Solubility Parameters

Number	Chemical	S_p	δD	δP	δH
1	Acetic anhydride	10.9	7.8	5.7	5.0
2	Acetone	9.8	7.6	5.1	3.4
3	Acetonitrile	11.6	7.5	6.3	6.3
4	Acetophenone	10.6	9.6	4.2	1.8
5	Acrylonitrile	12.1	8.0	8.5	3.3

6	Aniline	12.0	9.8	3.6	6.0
7	Benzaldehyde	10.5	9.5	3.6	2.6
8	Benzene	9.2	9.2	0.0	0.3
9	1,3-Butanediol	14.2	8.1	4.9	10.5
10	1-Butanol	11.3	7.8	2.8	7.7
11	2-Butoxyethanol	10.2	7.8	2.5	6.0
12	Carbon disulfide	10.7	10.7	0.0	0.3
13	Carbon tetrachloride	8.7	8.7	0.0	0.3
14	Chloroform	9.3	8.7	1.5	2.8
15	Cyclohexanol	11.0	8.5	2.0	6.6
16	Cyclohexanone	9.6	8.7	3.1	2.5

(table continued on next page)

(Continued)

Table 3

Number	Chemical	Sp	δD	δP	δH
17	Dichloromethane	9.9	8.9	3.1	3.0
18	Diethylenetriamine	12.6	8.2	6.5	7.0
19	1,4-Dioxane	10.0	9.3	0.9	3.6
20	Dimethyl formamide	11.6	8.3	6.7	4.5
21	Dimethyl phthalate	10.8	8.3	6.5	2.4
22	Epichlorohydrin	10.7	9.3	5.0	1.8
23	Ethanol	13.0	7.7	4.3	9.5
24	1-Ethanolamine	15.4	8.4	7.6	10.4
25	2-Ethoxyethanol	11.5	7.9	4.5	7.0
26	2-Ethoxyethanol acetate	9.6	7.8	2.3	5.2
27	Ethyl acetate	9.0	7.4	2.6	4.5
28	Ethylene carbonate	14.5	9.5	10.6	2.5
29	Ethylene chloride	10.1	9.3	3.3	2.0
30	Ethylene glycol	16.1	8.3	5.4	12.7
31	Formamide	17.9	8.4	12.8	9.3
32	2-Furaldehyde	11.9	9.1	7.3	2.5
33	Furfuryl alcohol	11.9	8.5	3.7	7.4
34	Glycerol	17.6	8.5	5.9	14.3
35	*n*-Heptane	7.5	7.5	0.0	0.0
36	*n*-Hexane	7.3	7.3	0.0	0.0
37	Ethylene cyanohydrin	15.1	8.4	9.2	8.6
38	*iso*-Octane	7.0	7.0	0.0	0.0
39	Methanol	14.5	7.4	6.0	10.9
40	Methyl ethyl ketone	9.2	7.7	4.4	2.5
41	4-Methyl-2-pentanone	8.4	7.6	3.0	2.0
42	1-Methyl-2-Pyrrolidinone	11.2	8.8	6.0	3.5
43	Methyl sulfoxide	13.0	9.0	8.0	5.0
44	Nitrobenzene	11.7	9.8	6.0	2.0
45	Nitromethane	12.8	8.2	9.0	3.8
46	2-Nitropropane	10.9	7.8	7.0	3.0
47	Octanol	9.9	7.9	1.6	5.8
48	3-Penanone	8.9	7.7	3.7	2.3

49	Propanol	12.1	7.8	3.5	8.5
50	Pyridine	10.7	9.9	3.2	2.2
51	2-Pyrrolinone	13.9	9.5	8.5	5.5
52	Toluene	8.9	8.8	0.7	1.0
53	1,1,1-Trichlooethane	8.6	8.3	2.1	1.0
54	Triethylene glycol	13.0	7.8	5.1	9.1
55	Xylene	8.8	8.7	0.5	1.5

Source: Adapted from Ref. 14.

works well only with homogeneous substances, usually in the absence of any supporting substrate. Less success has been achieved in characterizing multilayer materials or laminates, since individually layers may be affected differently [15,17,18].

B—
Application of Test Data

Chemical degradation by itself cannot fully demonstrate product barrier performance against chemicals. This form of chemical resistance testing does not ascertain the barrier properties of materials. While a material that shows substantial effects when exposed to a chemical can be ruled out as a protective membrane, it remains uncertain whether materials that show no observable or measurable effect provide a barrier against the test chemical. For this reason, chemical degradation data are typically used as a screening technique to eliminate a material from consideration for further chemical resistance testing (i.e., penetration or permeation resistance) [6,19].

To better understand the application of chemical degradation resistance data, it is instructive to know how this data is now being used within the protective clothing industry and how it could be used in a comprehensive material evaluation program.

1—
Current Protective Clothing Industry Practices

Within the chemical protective clothing and related apparel industries, a great deal of chemical degradation resistance data has been generated and is presented in various product literature. Unfortunately, most presentations of material chemical degradation resistance are based on qualitative ratings such as "excellent," "good," fair," "poor," and "not recommended." Ratings of this type provide little information to the end user, particularly when the basis of the ratings are not explained or cannot be related to a particular application.

Manufacturers that use degradation data often base their ratings on either observed visual changes or weight gain. In a few cases, tensile or breaking strength differences are also used to qualify material chemical degradation. Ratings are then based on arbitrarily set levels of degradation. One manufacturer uses the following scale for its degradation rating system:

Rating	Percent weight change
Excellent	0–10%
Good	11–20%
Fair	21–30%
Poor	31–50%
Not recommended	Over50%

This scale and probably all other rating systems used in the market have little bearing on the selection and use of protective clothing materials. Their presentation simply helps the end user to compare chemical effects on different materials. Since there is no one standard test method used in the industry for measuring chemical degradation resistance of protective clothing materials, chemical effect information cannot be compared from one source to the next because different test approaches and criteria are used [19].

The majority of chemical degradation resistance data is reported in the glove industry. This is because most gloves are made from elastomeric materials. As a class of materials, elastomers, when compared to plastics, show greater affinity for chemical adsorption and swelling [20]. Therefore, elastomeric materials are generally more susceptible to measurable chemical effects. This is particularly true today, because the majority of garment materials are composed of different plastic layers that have few observable degradation effects.

2—
Recommended Use of Degradation Testing

Chemical degradation resistance testing is best used to qualify material candidates for subsequent barrier forms of chemical resistance testing. Materials that show significant signs of chemical degradation as determined by relevant criteria can be eliminated from further consideration in the required application. The premise for using degradation testing in this fashion is to configure the test and choose criteria that reflect how the material will be used and what barrier performance should be demonstrated. Establishment of a degradation testing protocol should include the following decisions:

- How long should the exposure be conducted?

- Should the exposure be one-sided or by complete immersion?

- What material properties should be measured?

- How should material specimens be handled following exposure?

- What criteria should be used for accepting or rejecting a material for a given chemical?

In general, the length of chemical exposure should be as long as the maximum duration for which chemical contact can occur or for the same period of time being used for the barrier test procedure selected. In some cases, longer exposure periods are used because the longer chemical contact can accentuate degradation effects that may be difficult to observe or measure.

Immersion offers the easiest approach for measuring chemical degradation resistance but may not be suitable for some materials. As described for ASTM D471 and D543 test methods, immersion-based degradation testing is best applied to homogeneous materials. Nevertheless, the ease of placing material specimens into a container filled with chemical can also be applied to more complex material to determine if separation of layers or substrate occurs as the result of the chemical exposure. The principle argument against immersion-based testing is that many products are typically exposed on their external surfaces only. This means that the substrate and different layers inside the material matrix are not likely to be exposed to chemicals unless the external surface is breached in some manner. For this reason, one-sided exposures are considered more realistic for the evaluation of protective clothing chemical degradation. On the other hand, one-sided degradation testing is more difficult to perform, usually limits the size of the material specimen for subsequent physical property testing, and may not provide any more information about the materials performance following chemical exposure.

Physical properties should be selected to measure a material characteristic of interest. For the use of degradation testing as a means for screening material chemical resistance, observable changes in specimen appearance and weight gain are suggested. While disintegration of a test specimen is an easily recorded event, other differences in the visual appearance of test specimens may not be easily discerned. When chemicals are darkly colored, it may be impossible to carefully examine the material. Furthermore, it is difficult to achieve consistent material performance determinations using visual observations as the sole basis for rating material chemical degradation resistance. Nevertheless, the use of visual observations offers the easiest approach for conducting degradation testing with a minimum of specimen handling. When used, operator comments should be confined to certain observations. Examples include:

- Discoloration (if the material is not darkly colored)

- Curling

- Swelling

- Delamination (for multilayer or fabric supported materials)

- Disintegration

Depending on both the nature of the chemical and material being evaluated, other "standardized" observation categories can also be created.

Measurement of weight change provides a simple, quantitative approach for assessing material degradation resistance. Material specimens may either gain or lose weight, depending on how the chemical interacts with the material. Weight gain is caused by adsorption or absorption of a chemical on or in the material specimen and is often evidenced by swelling. Specimen weight loss is primarily due to some disintegration of the material or removal of particular components, such as plasticizers and other additives. In some cases, both phenomena can occur and result in very little weight change, even though significant material effects have occurred. Weight change is always indicated as the percent change based on the sample's original weight.

Chemical degradation resistance testing involving the measurement of weight change is often affected by the techniques used for specimen handling. This handling can remove chemical from the material's surface. In addition, removal of the material specimen from the chemical allows evaporation of volatile chemicals both off the surface and from inside the material matrix. The design of a degradation testing procedure must include uniform specimen handling techniques to avoid systematic errors. Each test method defines slightly different procedures:

- ASTM D471 specifies quickly dipping the specimen in acetone, blotting with a lint-free blotter paper, and then placing it in a tared, stoppered weighing bottle.

- ASTM D543 requires similar handling but indicates that the rinsing should be done with water, acetone, or not at all, depending on the exposure chemical.

- ASTM F1407 uses blotting only (without any sample rinsing).

The choice of specimen handling procedures should be based on the nature of the chemical being testing and may need to be different for different chemicals, particularly when both low-vapor-pressure, nonvolatile and high-vapor-pressure, volatile chemicals are tested. The former class of chemicals should require some blotting, with the time between removal from the chemical and weighing not as critical. Handling of specimens that have been exposed to high-vapor-pressure, volatile chemicals will most likely dictate no specimen rinse and a uniform period between specimen removal and weighing.

Development of screening criteria should be based on experience with the material(s) being evaluated and the barrier test chosen for assessment of chemical resistance. For example, small weight changes in some materials, such as Teflon or polyethylene laminates, may provide a clue of rapid permeation. But for other types of materials, these changes may not be significant for their permeation resistance. Whether the material specimen includes substrate fabric can also be a factor insetting acceptance and rejection criteria. Some fabrics can readily absorb test chemicals, particularly when immersion-based testing is used. If degradation testing is performed for screening materials prior to penetration resistance testing, then only severe material changes that could lead to penetration of liquids through the material of interest need be considered.

The last consideration for using chemical degradation resistance testing is economic. The costs of the tests for degradation screening combined with subsequent barrier tests should not exceed the cost of barrier testing alone with all material and chemical combinations.

The other use for chemical degradation resistance testing is to identify potential modes of a product's failure. This form of degradation testing is most suitable to nonplanar components such as seams, closure, gaskets, or any other accessories used on the product. The chemical performance of these items can be evaluated by degradation tests that combine chemical exposure with an appropriate physical property test. Some examples include:

- Evaluation of rigid-formed materials for environmental stress cracking (see ASTM D1975)

- Assessment of transparent material clarity following chemical exposure using light transmittance and haze testing (see ASTM D1003)

- Measurement of changes in seam or closure strength (see ASTM D751 for robber materials or coated fabrics, D1683 for textiles, and F88 for plastic materials)

- Operability of zippers (see ASTM D2062)

- Hardness of product gaskets or interface materials (see ASTM D2240)

Overall, chemical degradation resistance testing can be a useful means for evaluating chemical barrier materials. However, it is important that the limitations of this testing be recognized and that decisions for barrier product selection and use never be based solely on chemical degradation resistance data.

III—
Penetration Resistance

In the U.S. protective clothing industry, the ASTM F-23 Committee has defined penetration as "the flow of chemical through closures, porous materials, seams, and pinholes and other imperfection in a protective clothing material on a non-molecular basis." This definition is intended to accommodate both liquids and gases, but all U.S., European, and international test methods focus on liquid penetration. Liquid suspended in air as aerosols and solid particulates can also penetrate protective clothing materials, but the discussion of penetration resistance in this chapter relates to liquids exclusively.

Much of the liquid penetration resistance testing pertains to water as the challenge. The ASTM D-11 Committee on Rubber and Rubber Products (which includes coated fabrics) defines water repellency, waterproofness, and water resistance for coated fabrics as follows:

- Water repellency—the property of being resistant to wetting by water

- Waterproofness—the property of impenetrability by liquid water

- Water resistance—the property of retarding both penetration and wetting by liquid waterLiquid repellency and penetration resistance are related, since wettability of the fabric affects the ability of the liquid to penetrate.

For porous fabrics, a liquid of surface tension γ will penetrate given sufficient applied pressure, p, when its pores are of diameter D, according the rela, tionship known as Darcy's law:

$$D = k\frac{4\gamma\cos\theta}{p} \tag{2}$$

where

θ = contact angle of liquid with the material

k = shape factor for the material pores

For nonporous fabrics, particularly coated fabrics or laminate materials, liquid penetration may still take place as the result of degradation. Given a sufficient period of contact, chemicals may cause deterioration of the barrier film to allow pathways for liquid to penetrate. In this sense, penetration testing allows an assessment of both material barrier performance to liquid chemicals and chemical degradation resistance.

There are two fundamentally different approaches used in liquid penetration resistance test methodologies: (1) "runoff-based" methods, and (2) hydrostaticbased methods. *Runoff-based techniques* involve contact of the liquid chemicals with the material by the force of gravity over a specified distance. The driving force for penetration is the weight of the liquid and the length of contact with the material specimen. Usually the material specimen is supported at an incline, allowing the chemical to run off, hence the name for this class of penetration tests. *Hydrostatic-based techniques* involve the pressurization of liquid behind or underneath the material specimen. It is this hydrostatic force that is the principal driver for liquid penetration. Though the term "hydrostatic" is used to describe this class of test methods, one of the tests in this class can accommodate a wide range of liquid chemicals.

Both classes of test methods are described next; however, specific discussion focuses on those test methods most generally used for assessing protective clothing chemical penetration resistance.

A—
Runoff-Based Test Methods

Runoff-based tests are characterized by three features:

- Impact of the liquid from a stationary source onto a material specimen

- Orientation of the material specimen at an incline with respect to the point of liquid contact

- Use of a blotter material underneath the material specimen to absorb penetrating liquid

Runoff-based tests differ in the distance separating the liquid source from the point of contact with the material specimen, the type of nozzle through which liquid is delivered, the amount of liquid and the rate at which it is delivered, the angle of the incline, and the type of test measurements made.

1—
Specific Runoff-Based Test Methods Available

There are a number of liquid penetration tests that are based on runoff techniques. These include:

American Association of Textile Chemist and Colorist (AATCC) Test Methods

- AATCC 42, Water Resistance: Impact Penetration Test

- AATCC 118, Oil Repellency: Hydrocarbon Resistance Test

European Community (CEN) Test Method

- EN 368, Protective clothing—Protection against liquid chemicals—Test Method: Resistance of materials to penetration by liquids

International Standards Organization (ISO) Test Method

- ISO 6530, Protective clothing—Protection against liquid chemicals—Determination of resistance of materials to penetration by liquids

U.S. Federal Government Test Methods (FTMS)

- FTMS 191A,5520—Water Resistance of Cloth; Drop Penetration Method
- FTMS 191A,5522—Water Resistance of Cloth; Water Impact Penetration Method
- FTMS 191A,5524—Water Resistance of Cloth; Rain Penetration Method

Table 4 provides a comparison of the key characteristics of each of the referenced test methods. It should be noted that some methods from different organizations are very similar to each other. These methods are also cross-referenced in Table 4.

As the rifles for several methods denote, the majority of these methods are intended for use with water as the liquid challenge only. Physically, many of the methods are suitable for testing with other liquids; however, the containment as-

Table 4 Characteristics of Runoff-Based Penetration Tests

Test Method	Type of Delivery	Liquid Amount and Rate	Sample Orientations	Measurement
FTMS 191A,5520	Polystyrene plate with 31 0.4-mm ID capillary holes 1.73 m above sample	Determined by test end point	45 Degrees, clamped onto perforated disk	Time to collect 10 ml water (from penetrating sample)
FTMS 191A, 5522	Spray nozzle at end of funnel with 19 0.89-mm holes 610 mm above sample	500 m	l45 Degrees, under 0.45 kg tension force	Weight of penetrating water
FTMS 191A,5524	Spray nozzle at end of funnel with 12 1-mm holes 305 mm above sample	300 sec at selected pressure head	Horizontal	Weight of penetrating wate
EN 368	Single, 0.8-mm bore hypodermic needle 100 mm above sample	10 ml at 1 ml/sec	45 Degrees, over blotter in semicircular "gutter"	Index of repellency; index of penetration
ISO 6530	Same as EN 368			

pects of these test methods vary and some are clearly inappropriate for use with hazardous chemicals.

The majority of test methods listed in Table 4 involve delivering relatively large quantities of water onto a sample and measuring the amount of water absorbed in a blotter paper placed underneath the material specimen. This approach is characteristic of AATCC 42, FTMS 191A,5522, and FTMS 191A,5524. Figure 7 shows a picture of a spray impact tested used in both AATCC 42 and FTMS 191A,5522. One method, FTMS 191A,5520, is used for materials where a significant amount of water is expected to penetrate since the time to obtain 10 ml of water is used as the test endpoint. The large quantities of water specified and the lack of containment in the design of the apparatus make these test methods unsuitable for other liquids.

AATCC 118 was designed to measure fabric resistance to oil. However, this test is a repellency type test, where surface appearance of the material specimen is rated after its exposure to selected hydrocarbons. This test is similar to several other tests in the literature involving water where either percent absorption of liquid by the fabric is measured or the pattern of wetness on the underside of the material specimen is rated on percent coverage.

Two of the test methods are essentially identical and are designated for use with various liquid chemicals. Both EN 368 and ISO 6530, the so-called "gutter test," use a system where the liquid chemical is delivered by a single, small-bore nozzle onto the material specimen at a distance of 100 mm (see Fig. 8). The material is supported in a rigid transparent gutter, which is covered with a protective film and blotter material set at a 45-degree angle with respect to the horizontal plane. A small beaker is used to collect liquid running off the sample. The two results reported in these tests are the indices of penetration and repellency. The "index of penetration" is the proportion of liquid deposited in the blotter paper:

$$\text{Index of penetration (P)} = \frac{M_p \times 100}{M_t} \qquad (3)$$

where

M_p = mass of test liquid deposited on the absorbent paper/protective film combination

M_t = mass of the test liquid discharged onto the test material specimen

The "index of repellency" is the proportion of liquid deposited in the blotter paper:

$$\text{Index of repellency (R)} = \frac{M_r \times 100}{M_t} \qquad (4)$$

where

M_r = mass of test liquid collected in the beaker

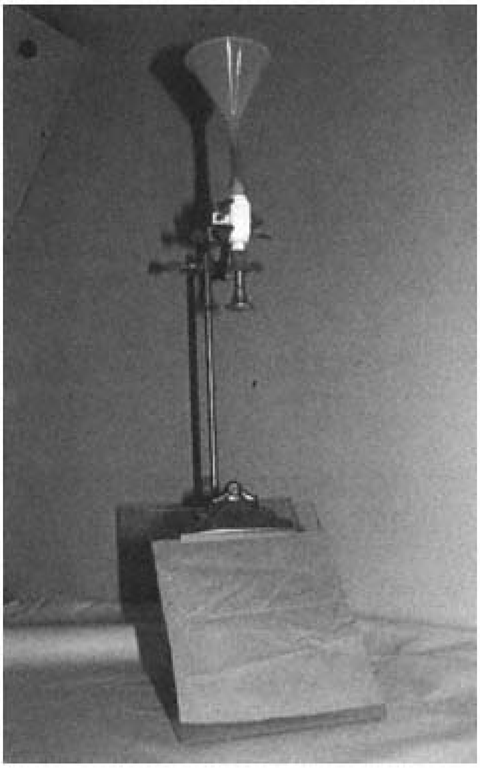

Figure 7
Spray impact tester used for testing
in accordance with AATCC 42 and
FTMS 191A,5222.
(Courtesy of TRI/Environmental, Inc.)

A mass balance of the liquid also allows calculation for liquid retained in the material specimen.

2—
Application of Runoff-Based Test Methods

Not all of the tests described so far can be considered "true" liquid penetration tests. Penetration with these procedures can only be characterized when some assessment or measurement of liquid passing through the material specimen is made. Typically this is done by examination of the blotter material, either visually or gravimetrically.

Runoff tests are generally used on textile materials that have surface finishes designed to prevent penetration of liquid splashes. Many of these tests easily accommodate uncoated or nonlaminated materials, since the driving force for liquid penetration is relatively low (when compared to hydrostatic-based test methods). As a consequence, runoff tests may be infrequently specified for chemical barrier-

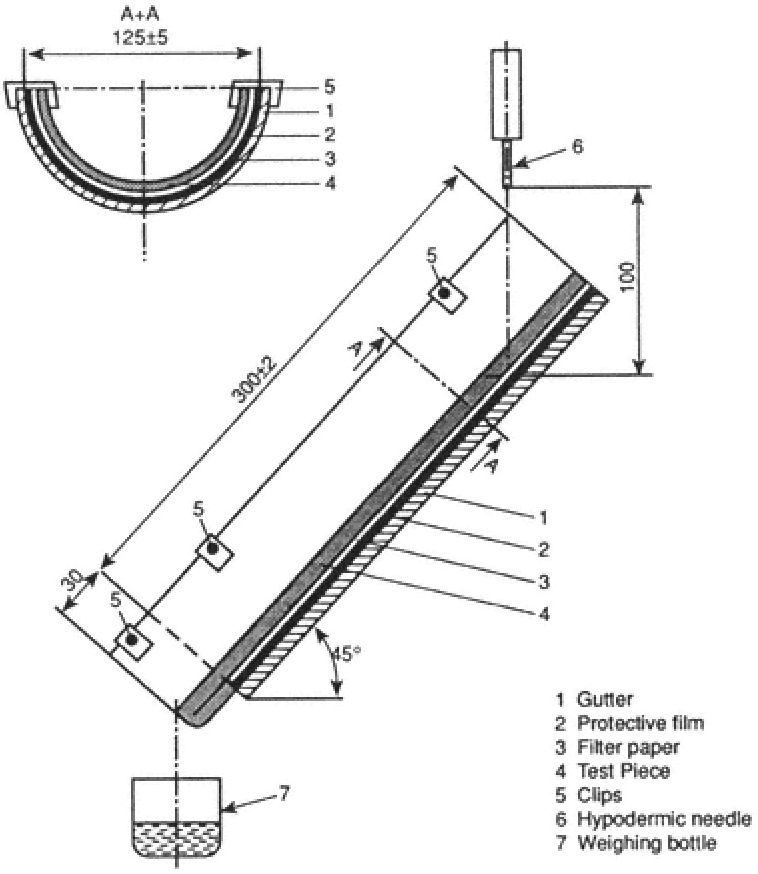

Figure 8
Specifications for CEN and ISO "gutter test."

based clothing. The European Community, while developing a range of chemical protective clothing standards, uses EN 368 in none but its lowest clothing classification (for partial body coverings). ISO 6530 is proposed as a test method for fire-fighting protective clothing in terms of evaluating composite materials against chemicals encountered in fire fighting. In the United States, only a few material manufacturers use runoff-based tests for characterizing the chemical penetration resistance of their fabrics. When used in this fashion, the fabrics tested are either uncoated or have thin simple plastic films.

3—
Specific Use of ISO 6530

Table 5 provides ranoff data on three different fabrics for selected chemicals using ISO 6530. One fabric has special surface finishes while another has a thin polyethylene coating. A third material involves a microporous film laminated to a non-woven fabric. From this testing, it is readily apparent that the test distinguished fabrics relying on surface finishes to prevent chemical penetration versus those that are coated or laminated with a film.

The relatively small amount of liquid involved in the test is not considered a strong challenge. For this reason, ISO 6530 contains very specific limitations for its use in testing chemical protective clothing: "Clothing which has been developed from materials selected by this method of test (i.e., ISO 6530) should only be used in well-defined circumstances when an evaluation of the finished item has indicated an acceptable level of performance." In other words, ISO recommends that the test be used only when the clothing item's overall integrity for preventing liquid penetration has been demonstrated.

Use of ISO 6530 is also subject to systemic errors. As with degradation tests described earlier, testing with volatile chemicals requires special handling procedures to minimize evaporation of solvent and its impact on test results. Likewise, test operators must be careful not to remove nonvolatile chemical through the handling of the blotter material.

The "open" nature of the test apparatus combined with its gravimetric basis may also be strongly influenced by environmental conditions. One testing laboratory has reported different results when tests are conducted in a hood versus those that are conducted on the laboratory bench (without ventilation) [21]. For these reasons, penetration testing using ISO 6530 should be performed with uniform handling procedures and in a controlled environment that is the same from test to test.

Some in the protective clothing industry do not consider any of the runoff tests as legitimate liquid penetration tests since these methods fail to demonstrate "liquidproof" performance for protective clothing material performance. In this

Table 5 Penetration Data for Selected Materials and Chemicals Using ISO 6530

Material	Chemical	Index of Penetration	Index of Repellency
Woven cloth	Ethanol	16.3	37.5
	1.6% Orthene™ in water	24.4	48.2
	13.3% Carbaryl in water	15.5	64.0
Coated nonwoven fabric	Ethanol	0.9	84.4
	1.6% Orthene™ in water	0.0	95.9
	13.3% Carbaryl in water	0.0	92.9
Microporous film laminated nonwoven fabric	Ethanol	0.6	88.4
	1.6% Orthene™ in water	0.0	95.4
	13.3% Carbaryl in water	0.02	92.5

context, liquidproof performance is often defined as the ability of the material to prevent liquid penetration under conditions representative of use, These researchers contend that runoff-based or repellency penetration tests are an evaluation of the surface wettability characteristics for material finishes, and thus not true barrier-oriented techniques.

B—

Hydrostatic-Based Test Methods

Another class of penetration test methods involves those based on hydrostatic techniques. In this testing approach, liquid is contacted with the material specimen, with at least some portion of the test period having the liquid under pressure. Different devices or test cells are available for providing this type of liquid contact with the material specimen, in essence representing the differences among representative test methods. Like runoff-based test methods, the majority of the industry tests are designed for use with water. Many of the devices described in this section cannot be used with other liquids or may even be damaged if anything but water is used in the respective tests.

1—

Specific Hydrostatic-Based Test Methods Available

There are a number of liquid penetration tests based on runoff techniques. These include:

American Association of Textile Chemist and Colorist (AATCC) Test Method

- AATCC 127, Water Resistance: Hydrostatic Pressure Test

American Society for Testing and Materials (ASTM) Test Methods

- ASTM D751, Methods for Testing Coated Fabrics, Hydrostatic Test
- ASTM D3393, Specification for Coated Fabrics—Waterproofness
- ASTM F903, Resistance of Protective Clothing Materials to Penetration by Liquids

International Standards Organization (ISO) Test Method

- ISO 8096, Rubber- or plastics coated fabrics water-resistant clothing—Specification—Part 1: PVC-coated fabrics; Part 2: Polyurethane- and silicone elastomer-coated fabrics

U.S. Federal Government Test Methods (FTMS)

- FTMS 191A,5512—Water Resistance of Coated Cloth; High Range, Hydrostatic Pressure Method
- FTMS 191A,5514—Water Resistance of Coated Cloth; Low Range, Hydrostatic Pressure Method
- FTMS 191A,5516—Water Resistance of Cloth; Water Permeability, Hydrostatic Pressure Method

Two different types of testing machines prevail for measuring hydrostatic resistance. AATCC 127, ISO 8096, FTMS 191A,5514, and FTMS 191A,5516 all use similar devices, where water is introduced above the clamped material specimen at a pressure controlled by water in a rising column. A mirror is affixed below the specimen to allow the test operator to view the underside of the specimen for the appearance of water droplets. Both the pressure and length of exposure are to be specified for the particular application. AATCC 127 and FTMS 191A,5514 define water penetration as the pressure when a drop or drops appear at three different places of the test area (on the specimen). When a specific hydrostatic head is specified, test results are reported as pass or fail. FTMS 191A,5516 also permits measurement of the amount of water penetration, collected from a funnel and drain hose underneath the material specimen (in lieu of the observation mirror).

ASTM D751, ASTM D3393, and FTMS 191A,5512 use a motor-driven hydrostatic tester (pictured in Fig. 9). Water contacts the underside of the material specimen, which is clamped into a circular opening. Increasing hydraulic pressure is applied to the clamped material specimen at a specified rate until leakage occurs. The pressure at which this leakage occurs is noted and reported as the test result.

Of the already listed tests, only ASTM F903 was developed for testing liquids other than water [22]. In this test method, a 70-mm-square material specimen is exposed on one side to the test chemical for a specified period of time using a special penetration test cell (see Figs. 10 and 11). The test cell is positioned vertically to allow easy viewing of the material specimen. During the chemical exposure, a pressure head may be applied to the liquid for part of the test period. Penetration is detected visually and sometimes with the aid of dyes or fluorescent light. The test is generally pass/fail; that is, if penetration is detected within the test period, the material fails. Observations of material condition following chemical exposure are also usually provided. Different test specifications exist for the amount of chemical contact time and pressurization.

2—
Application of Hydrostatic-Based Test Methods

Penetration resistance using hydrostatic-based test methods can accommodate different types of material and clothing test specimens, including:

- Plastic or rubber films
- Coated fabrics
- Textiles
- Microporous films
- Clothing seam samples
- Clothing closure samples

For these types of material specimens there are different modes of failure. Continuous film or film coated fabrics generally only fail due to:

- Imperfections in the material, such as cuts or pinholes
- Deterioration (degradation) of the film, providing an avenue for liquid penetration

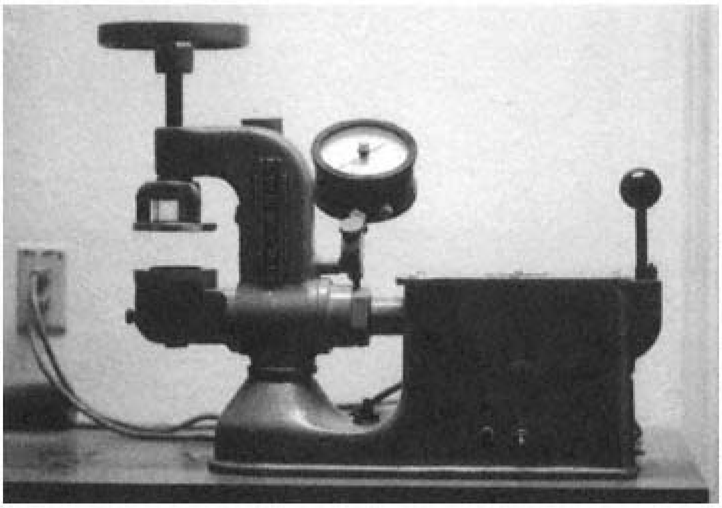

Figure 9
Mullen hydrostatic tester.
(Courtesy of TRI/Environmental, Inc.)

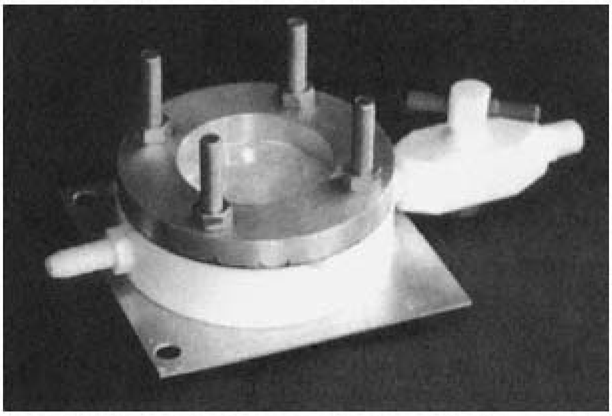

Figure 10
ASTM F903 penetration test cell.
(Courtesy of TRI/Environmental Inc.)

The latter type of failure often depends on the thickness of the film or coating as well as the contact time and amount of pressure applied to the specimen.

Textiles and microporous film products provide another set of possible failure mechanisms. Textiles may be considered as liquid barriers when they have been treated with water/chemical-repellent finishes. The ease of liquid penetration

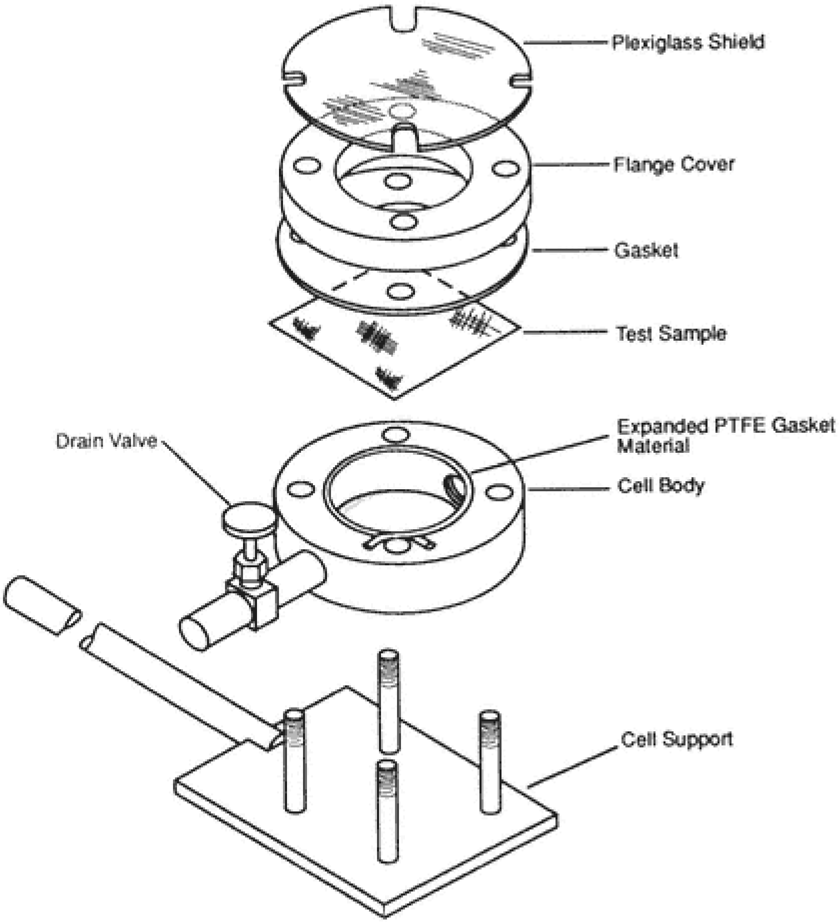

Figure 11
Exploded view of ASTM F903 penetration test cell.

is therefore more a function of repellant finish quality and the surface tension of the liquid being tested. Table 6 provides the surface tension of the liquid chemicals in ASTM F1001. Also, penetration may still be the result of material degradation while in contact with the chemical.

Microporous film products represent a unique class of test materials since by design they afford transmission of vapors but prevent liquid penetration. These materials therefore require careful observations since significant vapor penetration may occur. Like textiles, surface tension may be a factor, though most microporous films have pore sizes that preclude penetration of most common liquids at relative low pressures (less than 12 kPa).

The integrity of seams, closures, and other clothing material interfaces is easily evaluated using penetration resistance testing [23]. Their uneven sample profiles must be accommodated through special gaskets or sealing techniques. For zipper closures, a groove can be in the test cell to provide a better seal on the protrading teeth portion of the zipper. In assessing penetration resistance for these items, failure may occur because of:

- Penetration of liquid through stitching holes in seams
- Solvation of seam adhesives
- Degradation of seam tapes or other seam components
- Degradation of materials joining seam, causing lifting of seam tapes or destruction of seam integrity
- Physical leakage of closures

Berardinelli and Cottingham [23] demonstrated the utility of this test on a number of material, seam, and closure samples as shown in Table 7. Understanding how clothing specimens may fail provides insight into identifying protection offered by the overall clothing item. The qualitative nature of the penetration test requires that test operators be familiar with failure modes so that they can correctly assess whether liquid penetration has or has not occurred.

3—
Specific Use of ASTM F903

Penetration testing per ASTM F903 provides a test for assessing the barrier performance of materials against liquid chemicals [24]. Though measuring specimen weight change is not required, this testing can also serve to measure material

Table 6 Surface Tensions for ASTM F1001 Liquids

Chemical	Surface Tension (dyn/cm)
Acetonitrile	26.6
Carbon disulfide	31.6
Dichloromethane	27.2
Dimethylformamide	36.2
Ethyl acetate	23.4
Hexane	17.9
Methanol	22.1
Nitrobenzene	43.3
Sodium hydroxide	103.0
Sulfuric acid	55.1
Tetrachloroethylene	31.8
Tetrahydrofuran	26.5
Toluene	27.9

Table 7 Penetration Resistance Data on Selected Materials, Seams, Closures, and Chemicals

Material	Component	Chemical	Result, 5 min	Result, 10 min
Saranex-Tyvek	Fabric	Water	Pass	Pass
		Isooctane	Pass	Pass
		MEK	Pass	Pass
		TCE	Pass	Pass
	Stitched seam	Water	Fail	Fail
	Taped seam	Water	Pass	Pass
		Isooctane	Pass	Fail
		MEK	Fail	Fail
	Zipper with flap	Water	Pass	Fail
		Isooctane	Fail	Fail
PVC coated cotton	Fabric	Water	Pass	Pass
		Isooctane	Pass	Fail
		MEK	Pass	Pass
		TCE	Pass	Pass
	Double-sewn, armored seam	Water	Pass	Pass
		Isooctane	Pass	Fail
		MEK	Pass	Pass
		TCE	Fail	Fail

Note: Based on overall 15-min exposure with first 5 min at ambient pressure and second 10 min at 13.8 kPa (2 psig) using ASTM F903. MEK, methyl ethyl ketone; TCE, trichloroethylene.
Source: Adapted from Ref. 23.

degradation since visual observations are required. Degradation of the material, in turn, may be a primary route for penetration by some chemicals. The difficulty in penetration testing lies in making a clear-cut determination of liquid penetration. Many high-vapor-pressure, low-surface-tension solvents spread thinly over the material and evaporate quickly. Therefore, actual liquid penetration may be difficult to observe even when enhanced by using dyes (Sudan III is recommended for most organic solvents). Still, the test serves as a good indicator of material performance against liquid contact or splashes. Since test length and pressurization periods depend on the selected procedure within the method, pass/fail determinations are discernible and easily define acceptable material—chemical combinations.

While ASTM F903 establishes clear, detailed procedures for measuring material penetration resistance, experience in laboratories dictate careful attention to several areas, which include:

- Problems with visually interpreting penetration
- The influence of contact time and pressurization on liquid penetration

a—
Interpretation of Liquid Penetration

As stated earlier, penetration is determined by the visual observations of the test operator. As such, this determination lends itself to the bias and experience of the individual test operator. In most cases, liquid penetration is obvious with the appearance of fine droplets of liquid over the entire specimen surface or from a specific surface defect (Figs. 12 and 13). Alternatively, if a material flaw exists such as a pinhole, liquid may appear at a separate point on the test specimen. The visual detection of penetration may not always be an easy determination. This is based on several potential problems in which liquid penetration may seem to occur but is actually the result of:

- A poor seal between test cell and material
- Wicking of material textiles that may be present on both sides of the material being tested

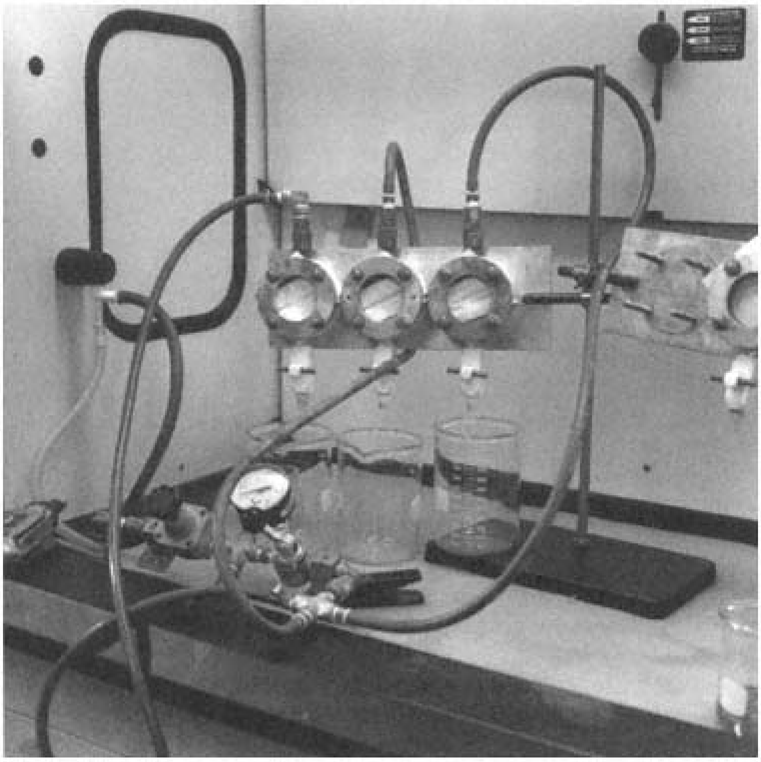

Figure 12
Overall ASTM F903 penetration test showing three
test cells operated in parallel.
(Courtesy of TRI/Environmental, Inc.)

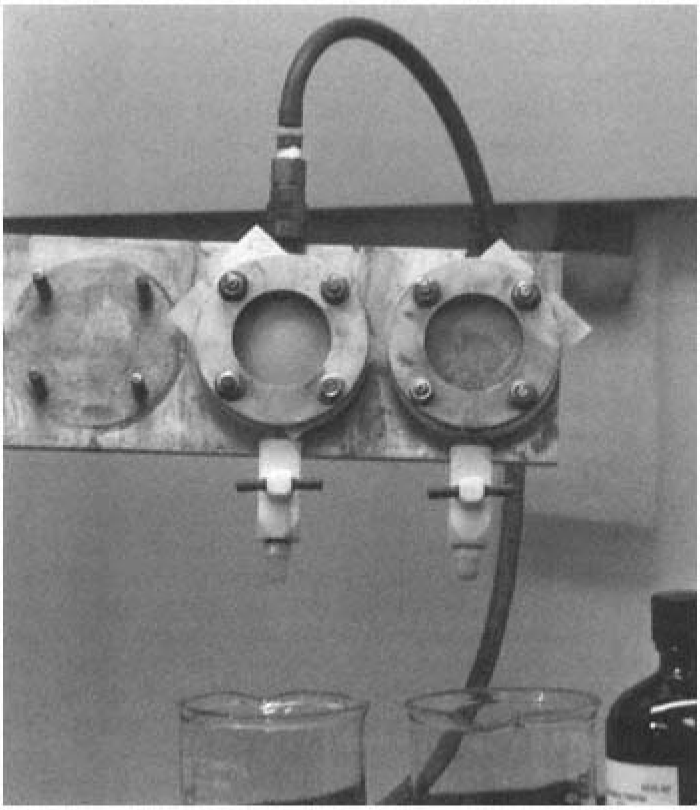

Figure 13
The penetration test cell on the right shows a pinpoint failure in the barrier material as evidenced by discoloration of the material surface.
(Courtesy of TRI/Environmental, Inc.)

- Penetration of liquid through some layers of the material specimen giving the appearance that the liquid is at the surface

- Vapor permeation through the sample with condensation of liquid on the Plexiglas shield of material surface

These situations would constitute "false positives." False negatives may occur when penetration occurs but goes undetected by the test operator. This can happen with high-vapor-pressure, low-surface-tension chemicals that spread thinly over the viewing side of the test specimen and evaporate quickly.

A number of practices can be implemented in penetration test programs that eliminate problems in detecting liquid penetration [25]:

- The test method already encourages the use of dyes to enhance visual detection of low-surface-tension, volatile chemicals. Sudan III works well with organic chemicals; red food coloring can be used for inorganic solutions, acids, and bases.

- Small droplets of test chemical can be placed on the inside (viewing) surface of the test material to determine how the chemical might appear when it does penetrate.

- Expanded polytetrafluoroethylene (PTFE) gasket material can be used in lieu of the standard rubber gaskets specified by the method to achieve better specimen sealing.

- For film products with textile fabrics on one or both sides of the material, specimen edges may be dipped in paraffin or wax to seal edges and prevent wicking.

- Blotting paper can be used to help determine if liquid does actually appear on the specimen viewing surface.

Leakage from a poor seal between the test specimen and cell may be evident by close observation of the viewing side of the material during the test. If leakage first occurs at the peripheral edge of the cell, this may be due to a poor seal or damage to the specimen due to compression of the sample at the sealing surface. This phenomenon is most likely to occur when the chemical is first added or at the beginning of any pressurization period. Failures of this nature should require repeating the test but can only be ascertained by careful observation of the test specimen during the test.

ASTM F903 provides the following criteria for interpreting liquid penetration:

- When a droplet of liquid appears or discoloration of the viewing side of the sample, or both; or

- Appearance of liquid or discoloration of the viewing side of the sample due to chemical permeation.

The practices just described help to determine the case of liquid penetration under the first criterion, but additional judgment is necessary when the penetration is the result of significant vapor permeation or penetration. The passage of chemical vapor through the material specimen may appear as condensation on the Plexiglas shield or on the material itself. Occlusion of the Plexiglas shield often inhibits observation of the sample. The Plexiglas shield itself is intended more as a safety feature than as a principal part of the test cell. Since the purpose of penetration testing is to determine material barrier effectiveness to liquids, only the appearance of liquid on the sample should be used for judging failure of the material. This mode of failure is best determined by applying blotting paper to the specimen viewing surface at the end of the test period.

Table 8 ASTM F903 Penetration Test Variations

Procedure	Initial contact period (minutes at 0 kPa)	Pressurization Period (minutes/pressure)	Subsequent contact period (minutes at 0 kPa)
A	5	10/1	None
B	5	10/2	None
C	5	1/2	54
D	60	None	None

b— Effect of Contact Time and Pressurization.

The most recent edition of ASTM F903 (1995) incorporates four types of contact time and pressure exposure formats (see Table 8). The original protocol consisted of exposing the material to the liquid for a five minute period at ambient pressure, followed by a 10-min period at 13.8 kPa (2 psig). This exposure condition was selected as a test pressure to simulate the force on a protective garment of a liquid coming out a burst pipe at an approximate distance of 3 m. A lower pressure of 6.9 kPa (1 psig) was adopted later on because many materials would "balloon" away from the test cell as pressure was applied. Some differences in material performance due to degradation effects have been noted as shown in Table 9 [22]. The new contact time/pressure formats in ASTM F903 were included to accommodate practices being used by the National Fire Protection Association in their requirements for chemical protective suit material and component penetration resistance [26].

The effects of pressure and contact time are important on the outcome of the test, and test specifiers should realize that differences in material performance can be expected when different contact time/pressure formats are chosen. How con-

Table 9 Effect of Contact Time and Pressure on Penetration of Selected Material—Chemical Combinations

Material	Chemical	Penetration test exposure protocol	Penetration time (min)
PVC/Nylon	Dimethylformamide	A	None
		B	None
		C	40
		D	50
Microporous film/ nonwoven laminate	Hexane	A	None
		B	5
		C	5
		D	None

tact time and pressure affect the test is dependent on the potential modes of failure as follows:

- Increased contact time allows for increased degradation of material samples.

- Increased pressure is more likely to enable detection of material imperfections in films, penetration of low-surface-tension liquids in textiles or breathable films, and location of construction or design flows in suit components (seams and closures).

Many unsupported film samples cannot be tested at high pressure since they burst when the pressure is applied. Severe "ballooning" of these test specimens in testing may also give questionable test results due to the relatively large forces placing the material in tension. In these cases, the true barrier properties of the material to liquid penetration are not tested. For this reason, the optional use of a screen having more than 50% open area has been specified in the latest form of the test method.

IV—
Permeation Resistance

Permeation involves a process in which chemicals move through a material at a molecular level. In the permeation process, chemical is first adsorbed on the external or exposure side of the material, then diffuses through the material, and finally desorbs from the other surface (interior or nonexposure side) as shown in Figure 14. As a consequence, the permeation process involves two fundamental modes of interaction with the material: the solubility of the chemical(s) in the

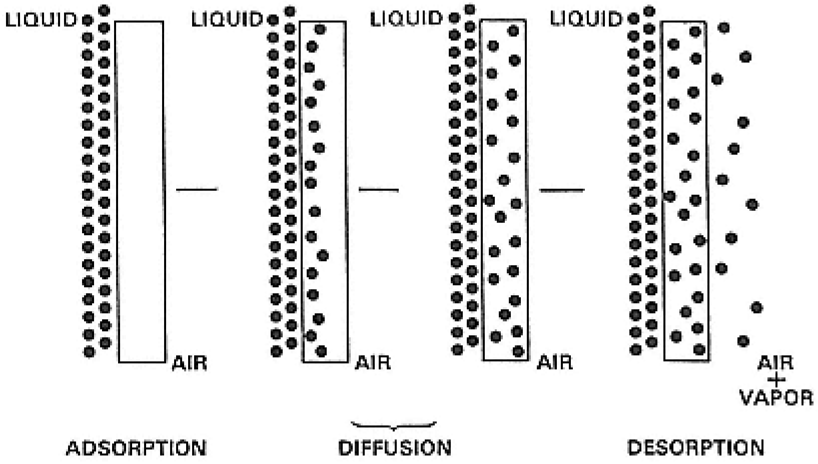

Figure 14
Illustration of the permeation process.

material, and the propensity for the chemical(s) to diffuse through the material. In some cases, chemical solubility may be of little importance, such as in the transmission of an inert gas through a thin polymer film. However, many chemicals do interact with the barrier materials, and material—chemical solubility is a significant factor for chemical permeation resistance [27].

Material permeation resistance is generally characterized using two test results: breakthrough time and permeation rate. Breakthrough time is the time when a chemical is first detected on the "interior" side of the material. As is discussed later, its determination is strongly dependent on how the test is configured and the sensitivity of the detector. Permeation rate is a measure of the mass flux through a unit area of material for a unit time. Permeation rate is most commonly expressed in units of micrograms per square centimeter per minute ($\mu g/cm^2$ min). For a given material—chemical combination, the steady-state or maximum observed permeation rates are reported.

Understanding permeation results requires some knowledge of the theory and factors that define material—chemical permeation behavior as well as the different approaches that can be used for its measurement.

A—
Permeation Theory

The permeation process can be modeled using the combination of theory for solubility and theory for diffusion. From solubility theory, two substances are soluble if, upon mixing, the free energy of the mixture is less than the sum of the free energies of the two pure substances. The free energy of mixing is defined as

$$\Delta G_m = \Delta H_m - T\,\Delta S_m \qquad (5)$$

where ΔG_m is the free energy of mixing, ΔH_m is the enthalpy of mixing, T is the temperature, and ΔS_m is the entropy of mixing. The significance of this equation is that enthalpy mixing term (ΔH_m) must be relatively small in order to have a negative difference in the free energy. The larger the negative difference, the better the solubility.

As previously explained, the molecular forces holding a liquid together include dispersion, polarity, and hydrogen bonding as governed by the relationship

$$C^2 = D^2 + P^2 + H^2 \qquad (6)$$

where C is the cohesive energy density, D is the dispersion parameter, P is the polar parameter, and H is the hydrogen bonding parameter [28]. The square root of the cohesive energy density is called the one-dimensional, or total, solubility parameter. The three energy components taken as a vector are commonly referred to as the three-dimensional solubility parameter. Holcombe [14], Henriksen [11], Perkins and Tippet [16], and Bentz and Billing [15] have applied solubility theory to the prediction of chemical permeation through homogeneous materials. Use of solubility theory alone to characterize permeation behavior of more complex materials has been less successful [29].

Diffusion is the random movement of molecules such that, given enough time, the distribution of molecules tends toward even concentration over space [20]. The mathematical equation that describes diffusion is Fick's law:

$$J = -D \frac{\partial C}{\partial X} \qquad (7)$$

where

J = rate of transfer per unit area

C = concentration of the diffusion substance

x = distance into the material

D = proportionality constant, called the diffusion coefficient

This equation assumes that rate of transfer through a unit area of material is proportional to the concentration gradient measured normal to the material.

The fundamental, one-dimensional, differential equation of diffusion, which can be derived from Fick's law by considering diffusion into and out of a volume element, is

$$\frac{dC}{dt} = D \frac{\partial^2 C}{\partial x^2} \qquad (8)$$

Equations (7) and (8) can be solved with various initial and boundary conditions to obtain explicit relationships for the permeation rate and cumulative mass permeated as a function of time [31]. The simplest set of conditions and assumptions include:

- At time zero, there is no chemical in the material.
- Upon exposure to the chemical, the external surface of the material immediately equilibrates with the chemical. This means that the surface of the material is at its saturation concentration, or solubility, S.
- The concentration of the chemical on the interior side of the material is maintained at essentially zero.
- The material—chemical solubility and diffusion coefficient remain constant (concentration and time independent).
- The material does not swell with chemical.

Under these conditions, the amount of chemical that permeates a material of thickness x at any time t is

$$M = Sx\left\{\left(\frac{Dt}{x^2}\right) - \left(\frac{1}{6}\right) - 2\sum\left[\frac{(-1)^n}{(n\pi)^2}\right]\exp\left[-(n\pi)^2\left(\frac{Dt}{x^2}\right)\right]\right\} \qquad (9)$$

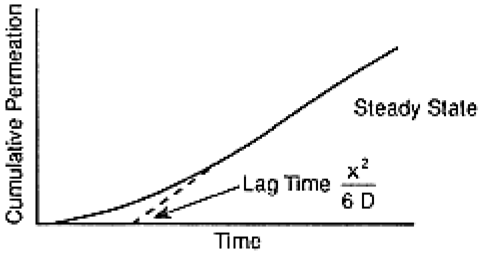

Figure 15
Theoretical plot of chemical concentration
versus time for the permeation process.
(From Ref. 38.)

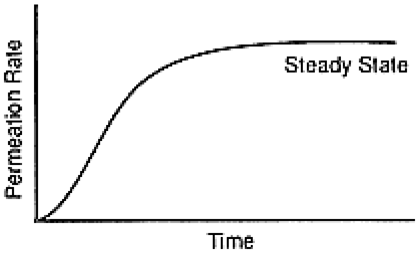

Figure 16
Theoretical plot of permeation rate
versus time for the permeation process.
(From Ref. 38.)

and the rate of permeation is

$$J = \left(\frac{SD}{x}\right)\left\{1 + 2\sum(-1)^n \exp\left[-(n\pi)^2\left(\frac{Dt}{x^2}\right)\right]\right\} \qquad (10)$$

Figure 15 shows the plot of cumulative permeation as a function of time using Eq. (9) whereas Figure 16 represents a plot of permeation rate versus time based on Eq. (10). The curve in Figure 16 is the first derivative of the curve in Figure 15. On Figure 15, the intersection of the slope for steady-state permeation with the x axis defines the lag time (T_1). This extrapolation can be mathematically determined, using the same conditions and assumptions, as follows:

$$T_l = \frac{x^2}{6D} \qquad (11)$$

Breakthrough time is not shown in Figures 15 and 16 because it is a function of several experimental parameters. Its determination is based not only on the test method used, but on the specific parameters of each test.

B—
Permeation Resistance Test Methods

The measurement of chemical permeation resistance is specified in different standard test methods offered by ASTM, CEN, and ISO:

American Society for Testing and Materials (ASTM) Test Methods

- ASTM E814, Test Method for Rubber Property—Vapor Transmission of Volatile Liquids
- ASTM D1434, Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting
- ASTM D3985, Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting using a Coulometric Sensor
- ASTM E96, Test Methods for Water Transmission of Materials
- ASTM F739, Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids and Gases Under Conditions of Continuous Contact
- ASTM F1383, Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids and Gases Under Conditions of Intermittent Contact
- ASTM F1407, Test Method for Resistance of Chemical Protective Materials to Liquid Permeation—Permeation Cup Method

European Community (CEN) Test Method

- EN 369, Protective clothing—Protection against liquid chemicals—Test method: Resistance of materials to permeation by liquids.
- EN 374-3, Protective gloves against chemicals and microorganisms—Part 3: Determination of resistance to permeation by chemicals.

International Standards Organization (ISO) Test Method

- ISO 2556, Plastics—Determination of the gas transmission rate of films and thin sheets under atmospheric pressure—Manometric method
- ISO 6529, Protective clothing—Protection against liquid chemicals—Determination of resistance of air-impermeable materials to permeation by liquids

These test methods may be segregated into two classes: vapor transmission tests and chemical permeation test methods. ASTM D481, ASTM D1434, ASTM D3985, ASTM E96, and ISO 2556 each represent gas or vapor transmission tests. Each of the techniques represented by these standards involve contact of the material's external surface with a gas or chemical vapor. In contrast, ASTM F739, ASTM F1383, ASTM F1407, EN 369, EN 374-3, and ISO 6529 are chemical permeation tests involving either liquid or gaseous chemical contact with the material and assessment of permeation as affected by both chemical solubility and diffusion through the test material.

1—
Vapor Transmission Tests

While vapor transmission may involve permeation, it may also be the result of vapor penetration. As a consequence, this testing is applied not only to continuous films but also to microporous films and uncoated textiles. The vapor transmission process is primarily governed by the diffusion of the gas or vapor through the material. Solubility effects are relatively small and in many cases insignificant.

Different techniques are used for the actual measurement of gas transmission rates in each of the preceding tests. ASTM D481 measures the vapor transmission of volatile liquids by placing the liquid in a test jar and allowing the vapor above the liquid to diffuse through a material that is mounted in the top of the jar. Loss of liquid is measured gravimetrically, and vapor transmission rates are reported in milligrams per square meter per second ($mg/m^2/sec$). ASTM E96 provides similar procedures for assessment of water vapor transmission, replacing the liquid with water, but also offers an alternative procedure involving desiccant inside the sealed jar and measurement of desiccant weight gain under carefully controlled temperature and humidity conditions. Both of these methods rely on the vapor pressure of the selected liquid and the relative concentration of the vapor exterior to the test cell as the driving forces for vapor transmission.

ASTM D1434, ASTM D3985, and ISO 2556 involve techniques where a difference is established between the partial pressures of the gas on either side of the membrane (material), usually by applying a slight vacuum on the interior side of the material. Each of these tests is intended for pure gases only and is typically applied in the assessment of packaging material permeation resistance. ASTM D1434 provides procedures for both manometric and volumetric determination of gas transmission. The gas transmission cell for manometric gas transmission testing is shown in Figure 17. ISO 2556 is equivalent to the pressure-based technique in ASTM D1434. ASTM D3985 is intended specifically for measuring oxygen gas transmission and entails the use of a coulometric sensor instead of differences in volume or pressure. Each of these standard test methods provide for measurement of gas transmission rate, permeance, and permeability. Permeance is the ratio of the gas transmission rate to the difference in partial pressure in the two sides of the film. Permeability is the product of the permeance and the film's thickness. The latter measurement is intended for homogeneous materials only.

2—
Chemical Permeation Tests

ASTM F739 was first established in 1981 as the first standard test method for measuring material permeation resistance to liquid chemicals [32]. ASTM F739, EN 369, EN 374-3, and ISO 6529 provide standardized procedures for measuring the resistance of protective clothing to permeation by chemicals using continuous contact of the chemical with the material's exterior surface. ASTM F1383 is a variation of ASTM F739 that involves testing under conditions of intermittent chemical contact. ASTM F1407 represents a simplified form of testing where

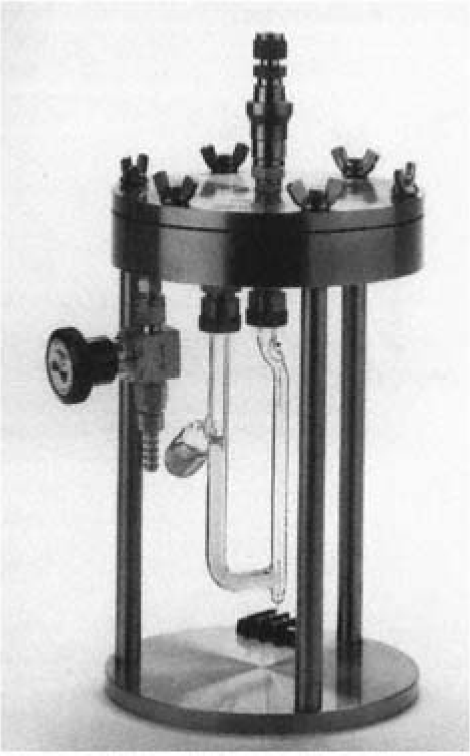

Figure 17
Manometric gas transmission cell for measuring gas transmission rates in accordance with ASTM D1434. (Courtesy of Custom Scientific Instruments).

permeation is determined gravimetrically. Based on its limited sensitivity, this method is primarily used as a screening test or field method.

In each of the tests (except ASTM F1407), a similarly designed test cell is used for mounting the material specimen. The test cell consists of two hemispherical halves divided by the material specimen. One half of the test cell serves as the "challenge" side where chemical is placed for contacting the material chamber. The other half is used as the "collection" side, which is sampled for the presence of chemical permeating through the material specimen. Figure 18 shows a conceptual illustration of the permeation test cell.

The basic procedure in each test is to charge chemical into the challenge side of the test cell and to measure the concentration of test chemical in the collection side of the test cell as a function of time. Of principal interest in permeation

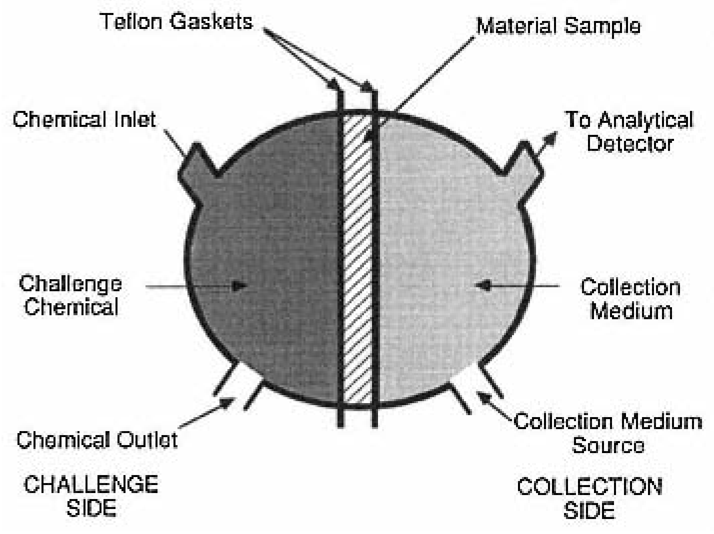

Figure 18
Conceptual diagram of a ASTM F739 permeation test cell.

testing are the elapsed time from the beginning of the chemical exposure to the first detection of the chemical (i.e., the so-called breakthrough time), the permeation rate, and the cumulative amount of chemical permeated. The results reported are dependent on the test method chosen:

- ASTM F739 requires reporting of breakthrough time and maximum or steady state permeation rate.

- ASTM F1383 specifies reporting breakthrough time and cumulative permeation.

- ASTM F1407 permits reporting either cumulative permeation or breakthrough time and permeation (maximum or steady state).

- EN 369 and ISO 6529 require reporting of breakthrough time with the total cumulative mass permeated at 30 and 60 min.

Other significant differences exist between the already listed test methods as described in the following section. Table 10 provides a comparison of key characteristics for each of the different permeation test methods.

C—
Parameters Affecting Permeation Resistance Testing

Although the permeation test procedure is simple in concept and generalized procedures are specified by each of the test methods already listed, a number of significant variations exist in the manner in which permeation testing can be conducted. These variables include:

Table 10 Differences Among Permeation Test Methods

Test method	Chemicals permitted	Type of contact	Collection medium flow rate(s)	Minimum test sensitivity (µg/cm^2 min)	Test results reported
ASTM F739	Liquids and gases	Continuous	50–150 ml/min	0.1	Breakthrough time Permeation rate
ASTM F1383	Liquids and gases	Intermittent	50–150 ml/min	0.1	Breakthrough time Cumulative permeation
ASTM F1407	Liquids only	Continuous	Not applicable	≈20.0*	Breakthrough time Permeation rate Cumulative permeation
EN 374-3	Liquids and gases	Continuous	50–150 ml/min	1.0	Breakthrough time Permeation rate
EN369	Liquids only	Continuous	520 ml/min (gas) 260 ml/min (liquid)	1.0	Breakthrough time Cumulative permeation at 30 and 60 min
ISO 6529	Liquids only	Continuous	520 ml/min (gas) 260 ml/min (liquid)	1.0	Breakthrough time Cumulative permeation at 30 and 60 min

*Depends on analytical balance, exposed specimen surface area, and time interval between measurements.

- The general configuration of the test apparatus.
- How the chemical contacts the material specimen in the test cell
- The type of collection medium used and frequency of sampling
- The type of detector and detection strategy used
- The test temperature
- The effect of multicomponent solutions

In addition, a separate class of materials—porous textile materials containing adsorbent particles—must be tested in totally different manner.

The variety of available test techniques and conditions allows several different approaches for conducting permeation testing and can provide different results for testing the same material and chemical combination.

1—

Test Apparatus Configuration

The overall test apparatus includes the test cell, chemical delivery system, and collection/detector system. This apparatus should be configured to meet testing needs and accommodate the characteristics of the chemical(s) being tested. Test cells are generally specified by the test method, but alternative designs are available and may be necessary for testing with specific chemicals or chemical mixtures. Likewise, the chemical delivery and collection/detection systems are dependent on the nature of the chemical and the requirements for running the test. Their selection is discussed later in this section. The way that each part of the apparatus is operated comprises the test apparatus configuration. There are two basic modes for configuring permeation test systems: closed-loop or open-loop. Aspects of test apparatus configurations are described next.

a—

Permeation Test Cells

ASTM F739 and ASTM F1383 specify a 51-mm (2.0-in) diameter test cell, which is constructed of two sections of straight glass pipe blown to meet the design shown in Figure 19. The two glass sections are joined by flanges on both sides, which are bolted together to provide a seal between the PTFE gaskets, glass sections, and material specimen. Collection and challenge sides of the test cell are configured to handle the types of chemicals being tested. When a liquid challenge is used, a single, relatively large inlet can be used, whereas gas challenges require both an inlet and outlet for charging gas into and out of the challenge chamber. Typically, collection sides of the test cell also contain an inlet and an outlet. When liquid is used as the collection medium, a stirring rod may be placed in one of these ports to affect uniform mixing of the collection medium with permeating chemical. Gas collection media require an inlet for charging gas into the test cell and an outlet that permits sampling near the material surface.

Both of these tests permit alternative test cells, as long as their equivalency can be demonstrated. Some laboratories use a small version of the test cell that

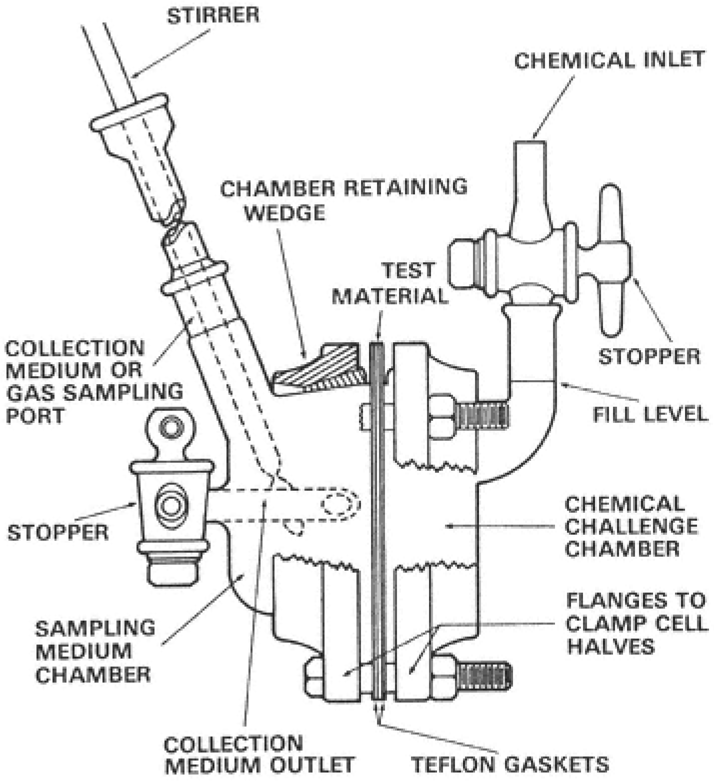

Figure 19
Specification ASTM F739 standard permeation test cell.

has a 25.4-mm (1.0-in) diameter (see Fig. 20). These smaller permeation cells use less chemical and minimize disposal problems, particularly for testing with hazardous chemicals. Billing and Bentz [33] and Henry [34] both investigated differences between the standard ASTM and smaller permeation test cells. Billing and Bentz [33] reported slightly longer breakthrough times for the 25-mm test cell but slightly better precision. Henry [34] concluded that there was no statistical difference in breakthrough times and permeation rates between the two permeation cells. The evaluation by Berardinelli et al. [35] of a different kind of glass permeation cell having a 30-mm exposure diameter compared favorably with the ASTM cell for determination of breakthrough time but yielded less precision in calculated permeation rates. Patton et al. [36] examined a proprietary stainless steel-constructed microcell to determine its equivalency with the ASTM standard cell. They found difficulties in traditional approaches to relate test performance

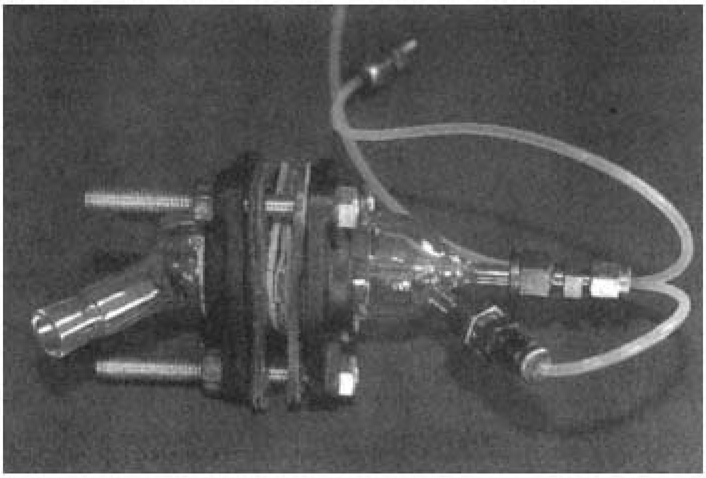

Figure 20
Small version of ASTM F739 permeation test cell having
25mm inner diameter exposure area.
(Courtesy of TRI/Environmental, Inc.)

and recommended using nonparametric statistics to evaluate the equivalency of permeation test cells.

While EN 374-3 specifies a similar cell as used in ASTM F739, EN 369 and ISO 6529 specify a 25-mm diameter exposure area with a cylindrical shape that is to be constructed of an "inert" material. Brass is recommended for gaseous collection media, while PTFE or glass is suggested for liquid collection medium. Unlike the ASTM test cell, the challenge side has a loose cover for adding the liquid challenge. This design of the test cell does not permit testing with chemical gases or vapors. Testing by one researcher has shown no significant differences, based on cell design alone, between CEN/ISO and ASTM test methods [37].

The test cell used for ASTM F1407 was mentioned as part of the discussion on degradation testing. This test cell is a shallow cup, usually fashioned out of metal coated with a PTFE film. An outer ring secures the material specimen onto the cup flange by a series of thumb screws. The side opposite the challenge side is open to the atmosphere as the test cell is inverted and placed either on a stand or elevated off of the testing surface [7,8] as depicted in Figure 21.

b—
Closed- Versus Open-Loop Permeation Systems

In closed-loop permeation systems, the volume of collection fluid is maintained throughout the test. This volume may be contained fully within the collection chamber or it may be circulated through the chamber, into a nonintrusive detector,

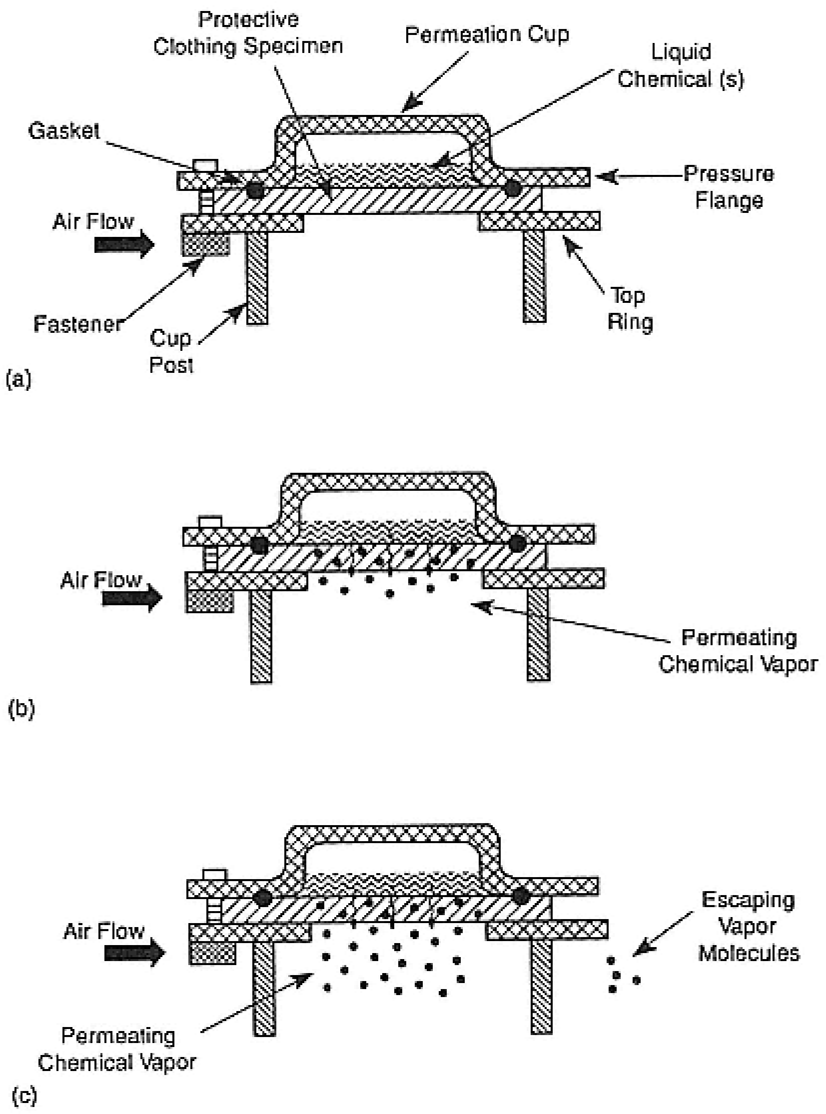

Figure 21
ASTM F1407 permeation test cup: (a) initial setup,
(b) chemicals begin to permeate material, and
(c) steady-state permeation.

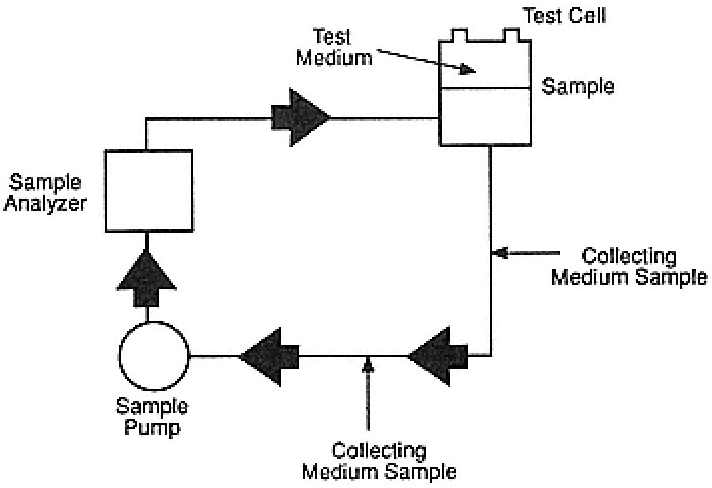

Figure 22
Closed-loop permeation test system configuration.
(From Ref. 35.)

and back into the chamber as illustrated in Figure 22. Since the total volume of collection medium remains constant, permeating chemical accumulates within the collection medium. In this system, the permeation rate must account for this accumulation of permeant as follows:

$$\text{Rate} = \frac{(C_n - C_{n-1})}{(t_n - t_{n-1})} \times \frac{V}{A} \qquad (12)$$

where

$(C_n - C_{n-1})$ = change in concentration of the challenge chemical between sampling periods

$(t_n - t_{n-1})$ = time between sampling periods

V = volume of collection medium

A = exposed area of the material specimen

In the open-loop permeation systems, a gas or liquid collection medium is passed through the collection side out of the test cell to the detection system (see Fig. 23). This collection medium stream can be evaluated discretely or continuously depending on the detector selected. Therefore, collection of permeant is specific to the sample taken (over a discrete time period), and permeation rates can be directly calculated as a factor of the collection medium permeant concentration (C) and flow rate (F):

$$\text{Rate} = \frac{C \times F}{A} \qquad (13)$$

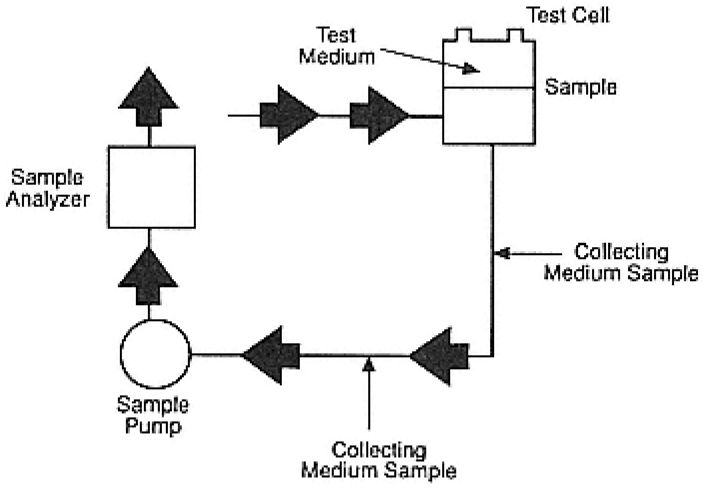

Figure 23
Open-loop permeation test system configuration.
(From Ref. 35.)

The choice of a closed- or open-loop system is most often determined by the properties of the chemical and the available detector. Some chemicals such as inorganic substances often require closed-loop systems, particularly if ion-specific electrodes are used that have recovery time constraints. Open-loop testing is preferred for many volatile organic chemicals because these systems can be easily automated as shown in Figures 24 and 25.

Both Henry [34] and Berardinelli et al. [35] examined differences in permeation test results for closed- and open-loop systems. For the small number of material—chemical combinations investigated, both researchers could not find appreciable differences in the collection medium in either breakthrough time or permeation rate. Schwope et al. [38] looked at intrinsic differences between closedand open-loop systems through a modeling approach based on the use of Fickian equations and assumed values for the diffusion coefficient, solubility parameter, and thickness of a material—chemical combination. In this treatment, they were able to show the effect of several system variables on permeation breakthrough time, including material thickness (assuming homogeneity), specimen exposed surface area, and detector analytical sensitivity.

2—
Methods for Chemical Contact

With the exception of ASTM F1383, each of the listed permeation test methods specify testing with neat chemicals under conditions of continuous exposure. Both EN 369 and ISO 6529 accommodate liquid chemicals only. In liquid exposures, the chemical or chemical mixture of interest is placed directly in the challenge por-

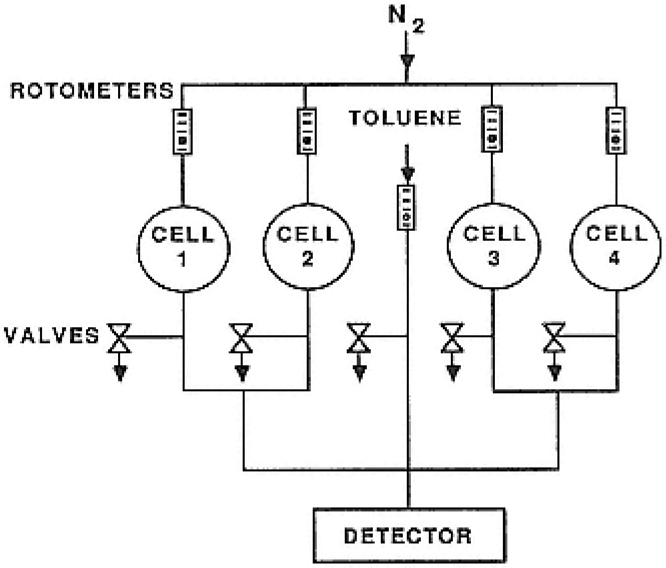

Figure 24
Design of an automated permeation test cell for testing of three samples and "blank" simultaneously. Each test cell is periodically monitored for permeating chemical by pressure switching of collection medium (dry nitrogen) flows to detector. Monitoring of "blank" test cell and toluene standard provide baseline and test system calibration, respectively.

tion of the test cell and left in contact with the material specimen for the selected duration of the test.

ASTM F739 and ASTM F1383 also permit testing with gases, using the modifications to the test cell as described earlier and the test system configuration pictured in Figure 26. When testing gases at 100% concentrations, time zero in the test is established by passing five volumes of the gas through the challenge chamber within a 1-min period. Following this initial period, the flow of gases is reduced to a rate that ensures the concentration of gas in the chamber does not change with time. Special considerations are needed for testing of gases to ensure integrity of the test cell and proper disposal of the effluent challenge gas [39,40].

Permeation testing may also be conducted against vapors of liquid chemicals per ASTM F739. These tests require a high level of temperature control to achieve consistency in the vapor concentration of the chemical and a different orientation of the test cell [39]. Most tests are performed with the chemical at its saturated vapor pressure at the test temperature using a test system configuration as shown in Figure 27. The test cell must be maintained in a horizontal position such that the air space above the liquid becomes saturated with vapor and the liquid does not

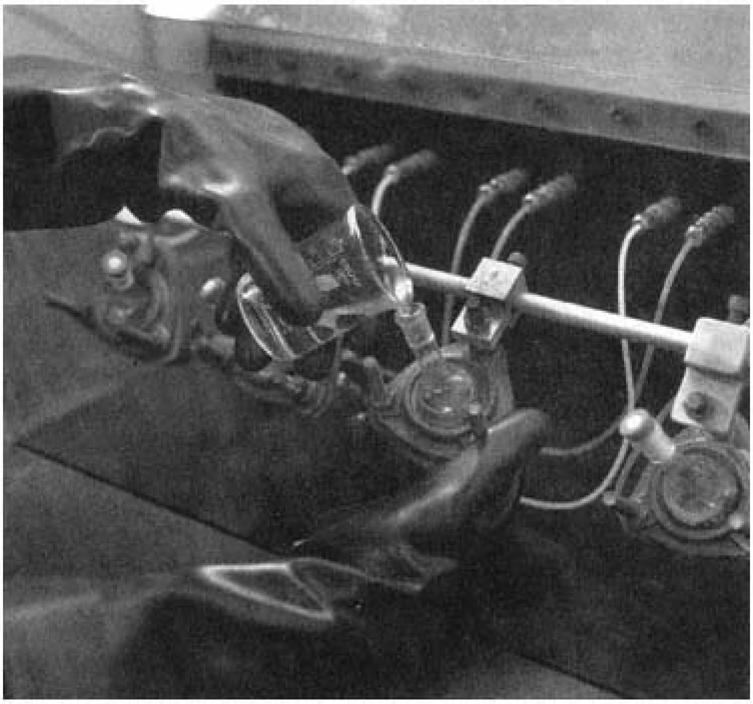

Figure 25
Automated permeation system.
(Courtesy of TRI/Environmental, Inc.)

contact the material specimen. Unfortunately, tests conducted in this manner may incur a relatively long transition time based on volatility of the test chemical. Table 11 show representative permeation data for two different material—chemical combinations as vapors.

Some research has also been reported for conducting permeation tests with a solid. Lara and Drolet [41] describe a modified test cell were a gel containing nitroglycerin was placed on the material's external surface for permeation testing.

Intermittent forms of chemical contact akin to splash-like exposures are prescribed in ASTM F1383. In this test method, the time of material specimen exposure to chemical is varied in a periodic fashion. Chemical is charged into the challenge side of the test cell and then removed after a specified time. This type of exposure may be repeated in a cyclic fashion. ASTM F1383 suggests three different exposure conditions as shown in Table 12.

The use of intermittent exposure conditions gives rise to permeation curves with a cyclic appearance (see Fig. 28). As a consequence, breakthrough time with cumulative permeation is reported in lieu of permeation rate for these tests. Schwope et al. [42] illustrated this behavior for a number of material—chemical

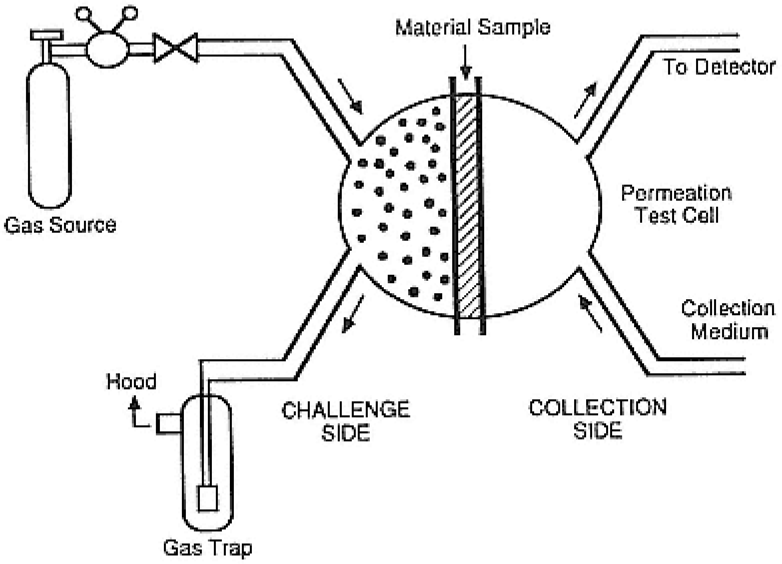

Figure 26
Configuration of permeation test system for evaluating gaseous chemical challenges.

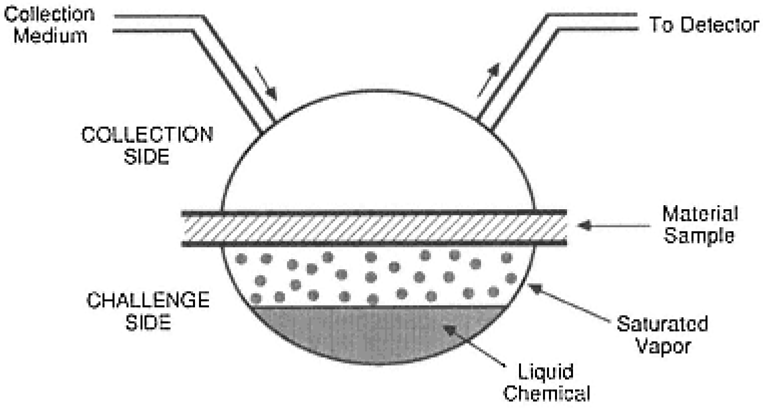

Figure 27
Configuration of permeation test system for evaluating chemical vapor challenges.

Table 11 Permeation Data for Chemical Vapors for Selected Material—Chemical Combinations

Material—chemical combination	Chemical challange	Breakthrough time (min)	Permeation rate (μ/cm^2 min)
Ethylene dichloride	Saturated vapor at 27°C	4	>25,000
against PVC glove	10 ppm in nitrogen	4	350
Dichloromethane	Liquid	16	470
against Viton-buty1	Saturated vapor at 27°C	28	280
suit material	100 ppm in air	No BT	Not applicable

Note:No BT, No breakthrough observed in a 3 h period for testing per ASTM F739.
Source: Adapted from Ref.39.

Table 12 ASTM F1383 Recommended Exposure Conditions

Condition	Contact time (min)	Purge time (min)	Number of cycles
A	1	10	10
B	5	10	7
C	15	60	3

combinations and found the cumulative permeation to be proportional to the relative exposure time. Man et al. [43] compared permeation breakthrough times of protective clothing materials against specific chemicals using liquid contact, liquid splashes, and vapors. Their findings showed significant differences between the different exposure conditions for some combinations of materials and chemicals, but lesser changes in breakthrough time for other material—chemical sets. They postulated that the different wetting characteristics of the test materials contributed to this phenomenon indicating those materials that easily wet by a chemical may show similar permeation for liquid splash exposures as with continuous liquid exposure.

3—

Types of Collection Media and Frequency of Sampling

Collection media should be chosen to reflect the permeating chemical being evaluated with its particular characteristics that affect acceptable levels of detection. Sampling of the collection medium is dependent on the chosen detector.

a—

Types of Collection Media

The collection medium must have a high capacity for the permeating chemical(s), allow ready mixing, be readily analyzed for the chemical(s) of interest, and have no effect on the clothing material being tested [44]. A collection medium's capacity refers to the relative amount of chemical that can be collected. Collection media with low capacities will hinder the detection of

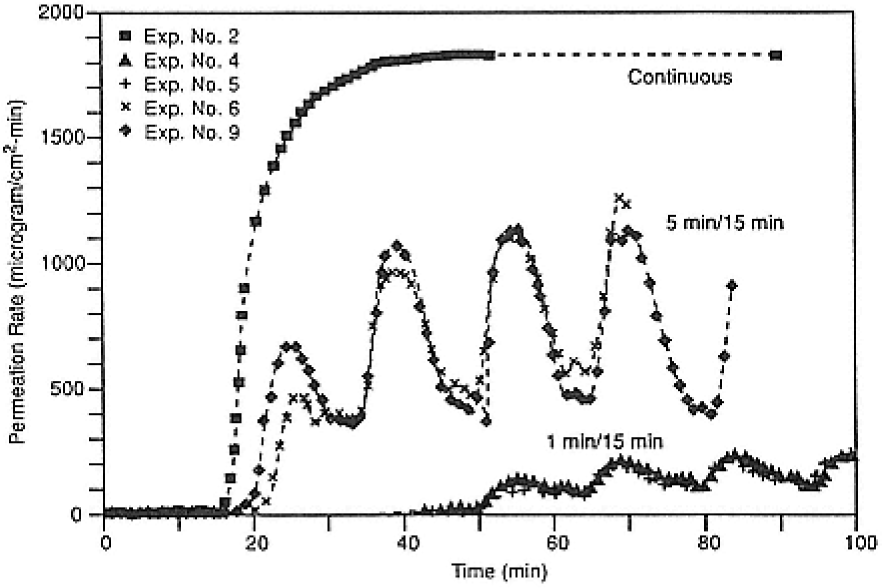

Figure 28
Cyclic permeation observed during permeation test involving intermittent contact.
(Adapted from Ref. 42.)

permeation, showing lower than actual permeation rates. Schwope et al. [38] recommended that the concentration of the permeant in the collection medium at the clothing/collection medium interface and in the bulk of the collection medium be maintained below 20% of the solubility of the permeant in the collection medium when the challenge is a neat chemical.

Air, nitrogen, helium, and water are common collection media. In general, these collection media have no effect on the clothing material and are amenable to most analytical techniques. Fricker and Hardy [45] developed a test method involving a saline collection medium to simulate sweat on skin.

In cases where the test chemical has a relatively low vapor pressure, gaseous collection media may have inadequate capacity for the permeant requiring a different choice of collection medium. Similar concerns arise for test chemicals having low water solubility when water is the collection medium. These situations may be addressed by circulating large volumes of fresh gas or water through the collection chamber; however, this practice will dilute permeant concentration in the collection medium and reduce test sensitivity.

Some test chemicals exhibit both low water solubility and vapor pressure. Chemicals with these characteristics generally include higher molecular weight chemicals such as polynuclear aromatics, polychlorinated biphenyls (PCBs), and some pesticides. One approach for conducting permeation tests with these chemicals has been to use solid collection media [42,46]. This technique involves placing a solid, highly absorbent film directly against the material specimen. Ehntholt [46] designed a special test cell successfully using a silicone rubber material for collection of pesticides. Unfortunately, this technique has also been reported to be very labor-intensive, involves multiple replicates to determine breakthrough times, and is subject to cross-contamination [44]. In addition, swelling of the test material can prevent uniform contact between the specimen and the solid collection medium. An alternative approach advocated by Pinnette and Stull [44] and Swearengen et al. [47] has been the use of a liquid splash collection. In these approaches, a solvent medium is briefly contacted with the material specimen on the collection side and the extract evaluated for the chemical(s) of interest. If such an approach is followed, it first must be demonstrated that the solvent does not affect the barrier properties of the test material. For example, the absorbance and back diffusion of the solvent from the collection medium into the clothing material could swell or soften the material and thereby promote more rapid permeation of the challenge chemical. A third approach was used by Spence [48] for permeation testing with halogenated pyridines. His method employed a technique for concentrating the permeant in the collection medium by use of a trap built with the detector gas chromatograph.

b—
Agitation of Collection Media

Agitation of the collection medium is recommended to ensure that it is homogeneous for sampling and analytical purposes, and to prevent or minimize concentration boundary layers of permeant at the interface of the clothing material and the collection medium. It may or may not be needed, depending on the medium chosen, the capacity of the medium for the test chemical(s), and the nature of the chemical challenge. ASTM F739 specifies a range of flow rates from 50 to 150 ml/min (ISO 6529 specifies a rate of 520 ml/min for gaseous collection media and 260 m/min for liquid collection media). Mixing is particularly important for closed-system testing. In open-loop systems, flow of the collection medium is Usually considered acceptable for test systems where the collection medium has high capacities. Agitation of the collection medium is recommended when the concentration of the permeant is above 20% of the partition equilibrium at the clothing/collection medium interface [38]. Testing with multicomponent chemical mixtures may also require agitation to maintain a constant concentration of the challenge at the mixture/material specimen boundary.

c—
Frequency of Sampling

Permeant sampling of the collection medium may be either continuous or discrete. Some permeation test system configurations permit continuous sampling of permeant in the collection media. In these systems, the permeant concentration or permeation rate can be constantly determined directly, providing the permeation curve for the test system. For closed-loop permeation systems, nondestructive analytical methods must be used for continuous sampling.

Other system configurations or test parameters dictate discrete sampling at periodic intervals dependent on the analytical detector chosen and its ability to recover prior to a new analysis. Alternatively, discrete samples may be taken for later analysis that affect the total number of separate analyses to be performed. Discrete sampling schemes may also be necessary to accommodate test systems that involve multiple test cells operated in parallel. Discrete samples influence the determination of breakthrough time, since breakthrough time must be reported at the time of the previous interval when permeant is found in a sample. For example, if discrete samples are taken at 5, 10, and 15 min and a permeant is detected in the 10-min sample, the permeation breakthrough time is 5 min in following the procedure established in ASTM F739. More frequent sampling may show the permeation breakthrough time to lie sometime between 5 and 10 min.

4—

Detection Strategies

The method for monitoring the collection medium for the permeating chemical is selected by the tester. In selecting an analytical detection method, the tester must consider its sensitivity and selectivity as well as its compatibility with the collection medium. Breakthrough time is totally dependent on the sensitivity of the detector. Breakthrough time has been analytically defined as a detector response twice the background level of the system. Background levels can be determined using a "blank" test cell, one that contains material, but not challenge chemical.

a—

Detector Sensitivity

The analytical method by itself may be very sensitive, but the sensitivity of the permeation test can be orders of magnitude less. For example, consider two tests performed with the same analytical instrument and detection limit but with different flow rates of collection media. The same permeation rate will produce a lower concentration of permeating chemical in the stream with the higher flow rate. Breakthrough will be detected at a later time for this test. In the extreme, if the flow rate were very high relative to the permeation rate, it is possible that breakthrough would go undetected. Figure 29 shows how different analytical sensitivities affect breakthrough time.

The detection of chemical breakthrough is highly dependent on the sensitivity of the analytical method. For this reason, ASTM F739 requires that the analytical sensitivity must be reported along with breakthrough time. Reporting of analytical sensitivity alone, however, is insufficient to allow interpretation of test results. The analytical sensitivity of the detector may have little or no relevance to test method sensitivity, which is defined by the analytical sensitivity, the surface area of the clothing material sample, and the collection medium flow rate (openloop systems) or volume (closed-loop systems).

In a simplistic analysis, the sensitivity of a gravimetric system, such as one described in ASTM F1407, shows the effect of these variables. In this case, the sensitivity of the balance, exposed surface area, and time interval between mea-

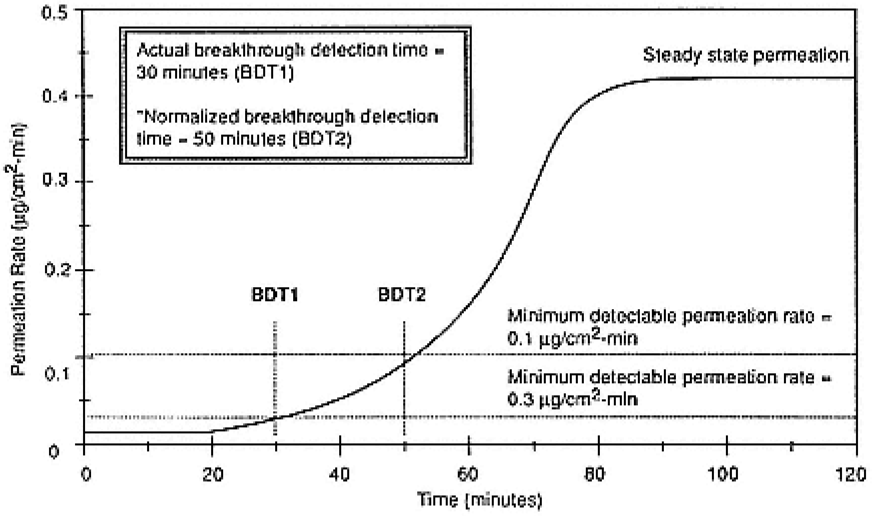

Figure 29
Impact of analytical sensitivity on interpretation of breakthrough time in permeation testing (actual versus normalized breakthrough detection time).

surements directly provide a means for determining the limited sensitivity of the test method using the following equation:

$$\text{Minimum detectable rate} = \frac{W}{(A \times t)} \qquad (14)$$

where W is the balance sensitivity in mass unit, A is the material surface exposure area, and t is the time between test measurements. Mickelsen et al. [49] showed good correlation with a gravimetric-based permeation test technique [50] as compared with gas chromatography using an infrared detector.

When analytical test measurements are made as part of the test procedure, more sophisticated procedures must be used to determine the sensitivity of the entire test system. ASTM F739 specifies a technique for measuring minimum detection limits (or minimum detectable permeation rates) based on a modified form of the test method itself. Verschoor et al. [51] developed a technique where a specialized permeation test cell has a collection side with an additional port, and aluminum foil replaces the material sample (see Fig. 30). No chemical is placed on the challenge side. The test chemical is injected near the surface of foil at a known rate using a syringe pump, and the detector response is determined and compared with a known detector calibration gas response. The concentration of chemical injected is successively increased to identify the lower limit of detection. The ratio of the detector response of the test chemical with the detector response of the

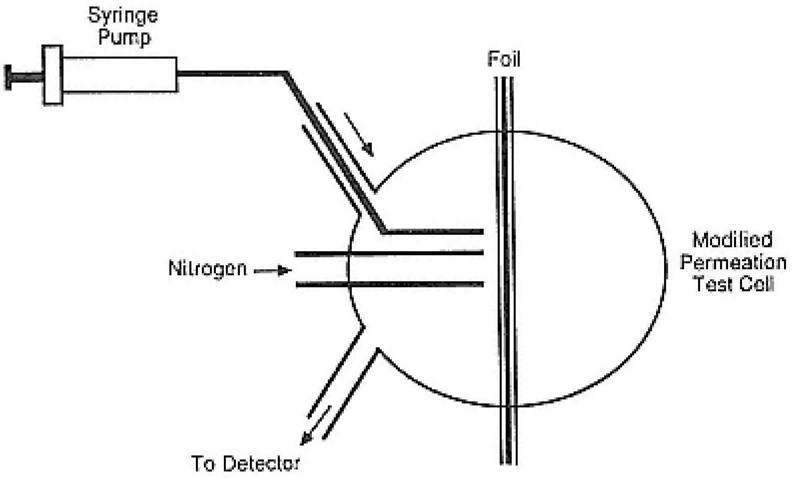

Figure 30
Design of specialized permeation test cell for measuring system detection limits.

calibration gas can then be used in subsequent testing with the selected chemical. This approach requires determining the test sensitivity for each chemical. Figure 31 shows how a blank cell, calibration gas (toluene), and specialized test cell can be integrated into an automated system for measuring minimum detection limits and permeation rates.

b—
Types of Detectors

Various detectors have been applied in tests for measuring the permeation resistance of materials. Since most inorganic chemicals involve some ionic potential, water is used as the collection media with Ph meters, ion-specific electrodes, atomic absorption, or ion chromatography used as the detectors. These systems are operated in a closed-loop mode.

Permeation tests involving volatile organic chemicals usually employ gas chromatograph detectors such as thermal conductivity, flame ionization, electron capture, or photoionization detectors. In most cases when gas chromatography is used, it is not necessary to use the column unless mixture permeation studies are being performed. Because these detectors are destructive in their analysis of the sample, they can only be used in an open-loop mode or closed loop if samples are withdrawn without replenishment of the collection medium. Perkins and Ridge [52] first described the use of infrared spectroscopy in permeation tests using a closed system test configuration. The advantage of this system is that it allows continuous recirculation of the collection medium through the detector and test cell. Similar systems have been used by Berardinelli et al. [35].

In tests involving nonvolatile, non-water-soluble chemicals, wipe samples of material interior surfaces, solid collection media, or liquid splash collec-

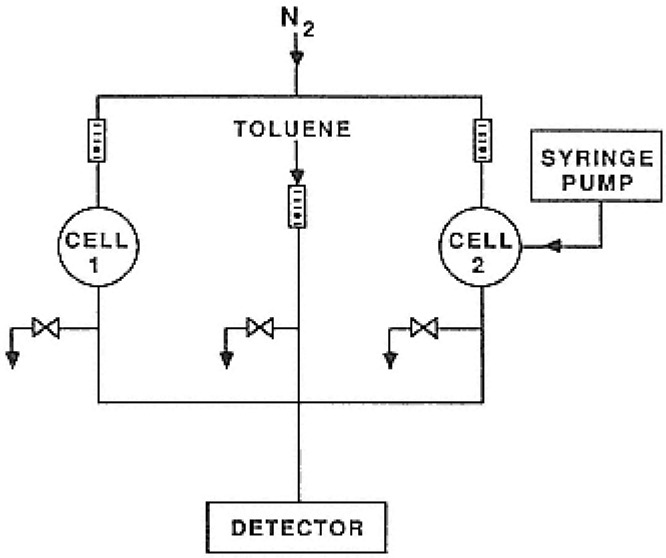

Figure 31
Configuration of permeation test system for measuring system detection limits.

tion aliquots are generally evaluated using either gas chromatography, highperformance liquid chromatography, or mass spectroscopy depending on the collection/extraction solvent used and the analytes being detected. Ehntholt et al. [46] used radiochemical labeling techniques for evaluating pesticide concentrations in isopropanol. Other techniques have been shown viable for difficult-to-evaluate chemicals by using small amount of collection medium [53] with ultraviolet (UV) spectroscopy.

It is important that the detector response remain linear within the range of chemical concentration to be evaluated. In some systems, rapid permeation at high rates can saturate the detector and provide meaningless data. Some laboratories have used sorbent tubes for collecting permeating chemical. This approach can also be used to determine the total or cumulative permeation when an open-loop test system is chosen, and allow for the separation and identification of specific components within challenge mixtures.

5—
Effects of Temperature

Spence [54] first showed significant changes in the permeation resistance of protective clothing materials with increasing temperature as evidenced by shorter breakthrough times and larger permeation rates. Changes in temperature may have an influence on permeation by several mechanisms. Increased temperatures may increase the concentration of the challenge chemical absorbed onto the material surface by increasing the solubility of the material—chemical matrix or by increasing the vapor pressure of the chemical [55] The rate-of-diffusion step in the permeation process may also increase with temperature following an Arrhenius equation type of relationship [54–58]. Temperature, therefore, exhibits its effect on breakthrough time and permeation rate through the diffusion coefficient (D) and solubility (S). The expected effect manifests itself in a logarithmic-like relationship between permeation rate and temperature. Figure 32 shows this relationship for several material—chemical pairs and temperatures. Zellers and Sulewski [59] modeled the temperature dependence of *N*-methylpyrrilidone through different gloves using Arrenhius corrections to both the diffusion coefficient and solubility originally proposed by Perkins and You [60]. Even small differences in temperature have been shown to significantly affect permeation breakthrough times as shown in Table 13. As a consequence, permeation testing must be performed under tightly controlled temperature conditions.

6—

Effect of Multicomponent Challenges

When permeation tests involve multicomponent chemical challenges, test configurations must employ detection techniques that permit the identification of each chemical in the permeating mixture. A number of researchers have investigated the effects of multicomponent chemical mixture permeation through barrier materials. Stampher et al. [61] investigated the permeation of PCB/paraffin oil and 1,2,4-trichlorobenzene mixtures through protective clothing. They used a small amount of isooctane in the collection medium to capture permeating PCBs. Schwope et al. [62] performed extensive testing with pesticides using different active ingredients and carrier solvents. Their tests demonstrated different breakthrough times and proportions of permeating chemicals between pesticide and carrier solvent. Bentz and Man [55] identified a case involving an acetone/hexane mixture where the mixture permeated a dual-elastomer-coated material at shorter breakthrough times than either of the pure components. This testing illustrated the potential synergistic permeation of mixtures. Mickelsen et al. [63] evaluated elastomeric glove materials against three different binary mixtures and found similar permeation behavior where mixture permeation could not be predicted on the basis of the individual mixture components. Ridge and Perkins [64] attempted to model mixture permeation using solubility parameters and found the technique to be only partially successful. Goydan et al. [17] were able to predict mixture permeation using a series of empirical rules when applied to a particular fluoropolymer laminate material.

7—

Evaluation of Adsorptive-Base Materials

Some materials may be designed to prevent the penetration or permeation of vapors by using adsorptive components within their structure. In general, these materials are intended for use in environments where only low levels of chemical

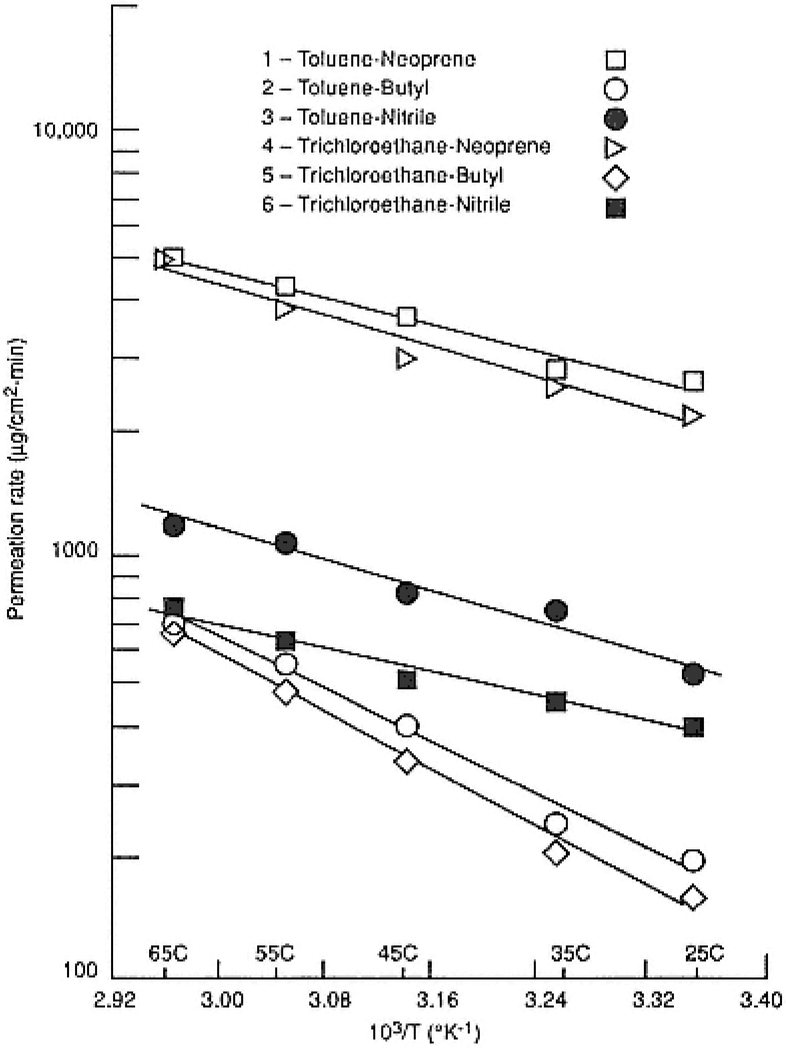

Figure 32
Plot showing effect of temperature on permeation rate for selected materialchemical combinations.
(From Ref. 58.)

concentration are to be encountered. The evaluation of these materials may be conducted in a fashion similar to that described earlier for gases or chemical vapors. However, these fabrics are typically evaluated by passing an air stream through the material in a technique similar to that used for assessing the service life of sorbent-based respirator cartridges [65–67]. One such technique is described by

Table 13 Selected Indications of Temperature Effects on Breakthrough Time

Test material	Temperature (°C)	Acetone breakthrough time (min)
Viton/chlorobutyl laminate	20	95–98
	26.5	43–53
Chlorinated polyethylene	22	32–35
	24.5	27–31

Source: Ref. 55

Baars, et al. [68]. Their technique involves measurement of fabric sorption rate and capacity by passing the challenge gas at a constant flow rate and concentration through the material with continuous detection of the effluent chemical concentration. When the concentration of the effluent is normalized to the inlet chemical concentration, the area above the curve for normalized concentration versus time represents the cumulative chemical adsorbed, while the area under the curve is that of chemical that has penetrated the fabric. Fabric saturation is reached as the normalized concentration approaches 1.

D—
Use and Interpretation of Permeation Testing

Of the chemical resistance data used in reporting protective clothing performance, the vast majority of test results are permeation resistance data. These data accompany most product performance data sheets and are provided in a number of data compilations [69–72]. However, a review of this data generally indicates that consistent comparison cannot be made and that suppositions for discerning material performance may not be properly based unless an understanding of the test conditions is realized. Much of the data is reported generically for material classes. Yet Michelsen and Hall [73] showed significant differences in chemical permeation through elastomers that were generically the same in composition and thickness. This illustrates that permeation data must be specific to the material—chemical combination being evaluated.

1—
Reporting of Permeation Data

As originally indicated, breakthrough time and steady-state or maximum permeation rate are typically provided as permeation test data. ASTM F739 as well as CEN and other test methods also require reporting of key test parameters. In general, these include a complete description of the test material, test chemical, and test system configuration. Table 14 lists test parameters that should be reported with each test. ASTM F1194, Guide for Documenting the Results of Chemical Permeation Testing on Protective Clothing Materials, provides a more extensive list of testing reporting requirements.

Table 14 Permeation Test Report Parameters

Area	Reporting requirements
Test chemical	Components
	Concentration
	Source
Test material	Identification
	Source
	Condition at time of testing
	Thickness
	Unit area weight
Test system	Overall configuration (open or closed loop)
	Type of test cell
	Type of challenge (continuous or intermittent)
	Collection medium
	Collection medium flow rate
	Detector or analytical technique
Test results	Breakthrough time
	Normalized breakthrough time
	Test system sensitivity
	Steady-state or maximum permeation rate
	Cumulative permeation

Since sensitivity significantly affects breakthrough times, ASTM, CEN, and ISO have adopted reporting requirements that are intended to normalize the effect of test system parameters on this measurement. Currently, ASTM F739 and ASTM F1383 specify reporting of the "normalized" breakthrough time in addition to actual breakthrough time. Normalized breakthrough time is defined as the time when the permeation rate is equal to 0.10 µmg/cm^2 min. International and European test methods specify reporting breakthrough times as the rate equals 1.0 µg/cm^2 min, a single order of magnitude difference from U.S. test methods. Therefore, it is important that permeation breakthrough time data be only compared when the respective sensitivities of the test laboratories are the same or if data is normalized on the same basis [74].

2—
Interpretation of Permeation Data

Permeation resistance testing is the appropriate test when vapor protection is required. This does not mean that the test can only be applied for gas or vapor challenges, but rather that the test discriminates among chemical hazards at a molecular level owing to the sensitivity for detecting permeating chemical in its vapor form (as opposed to liquids or solids). As such, permeation testing represents the most rigorous of chemical resistance test approaches.

Within the protective clothing industry, many end users judge the acceptability of a material on the basis of how its breakthrough time relates to the expected period of exposure. Reporting of permeation rate offers a more consistent and reproducible means of representing material permeation. The inherent variability and test system dependence on breakthrough times make these data a less then satisfactory choice for characterizing material performance. Permeation rate data can be used to show subtle changes in material characteristics and determine cumulative (total) permeation when acceptable "dose" levels of the test chemical can be determined. On the other hand, some material-chemical systems take a long time to reach steady state or exceed the capacity of the detector. In addition, the lack of widespread data on acceptable dermal exposure levels for most chemicals leads many specifiers to rely on breakthrough times exclusively.

The flexibility of most permeation tests allows testing laboratories to choose those conditions that best represent the expected performance of the material. Usually, the primary decisions in specifying permeation test involve the following:

- The chemical and its concentration
- The state and periodicity for contacting the chemical with the material
- The material and its condition prior to exposure
- The environmental conditions of the exposure
- The length of the test
- Sensitivity of the test system

The majority of permeation tests in the protective clothing industry are conducted using neat chemical continuously contacting pristine material at room temperature for a period of 8 h. Test sensitivities are at 0.10 $\mu g/cm^2$ min or better but may be higher for difficult-to-evaluate chemicals. Other barrier materials are generally evaluated against chemicals for longer period of times at slightly elevated temperatures for examining steady-state permeation rates and cumulative permeation. These test conditions are considered worst case, because constant contact of the material with the chemical is maintained, which may or may not be representative of actual use. When specific barrier product applications are identified, it is best to model the conditions of use through the selection of test parameters. If general performance is to be determined, using industry practices for test setup is preferred so that material performance may be compared against other available data.

V—
Recommended Testing Approaches

As products differ, so must the test strategies that are designed to evaluate barrier material characteristics of these products. Obviously, different tests are needed to evaluate different products based on how they are designed, what performance is intended, their required durability, and the expected application. The requirements for conducting barrier testing arise from several needs:

- Demonstrating product distinctive advantages (marketing)

- Meeting customer needs or demands

- Complying with appropriate standards

- Determining the viability of new products

- Documenting product quality control

While quality design and fabrication of product clothing items are paramount to offering a good product line, the majority of testing efforts are directed to evaluating the materials used in the construction of barrier products. This is partly because whole product performance may be difficult to assess in simulated "use" tests.

The use of standardized test methods provides advantages over in-house procedures. The latter procedures are often simple in design, done internally, and not always reproducible. Manufacturers tend to choose those methods that best represent their product's performance. Comparison of product performance on this basis is virtually impossible. Acceptance and use of ASTM and other recognized standards overcomes these problems and helps end users in their evaluation of product performance.

A—
Selection of Test Methods to Characterize Barrier Methods

The appropriateness of a specific chemical resistance test is dependent on the product's application and expected performance. The test selected should also consider the nature of the material to be evaluated. Some materials should not be evaluated in certain barrier tests, because the methods do not allow for discriminating their performance [75].

- Degradation testing may show how product materials deteriorate or are otherwise affected, but will not always demonstrate retention of barrier characteristics with respect to specific chemicals. Degradation testing is most useful when retention of specific physical properties (e.g., strength) is desired or as a screening technique for other chemical resistance (barrier) tests. This type of testing may be applied to all types of materials.

- Runoff-based penetration testing should only be used if the wetting or repellency characteristics of material surfaces are to be evaluated. Like degradation testing, runoff-based penetration testing does not offer an adequate assessment of material barrier performance. This testing approach can be used with all types of materials, but is best applied to textile materials or lightly coated fabrics for determining surface finish characteristics.

- Hydrostatic-based penetration tests are designed to evaluate water or chemical barrier performance of materials, Only ASTM F903 allows testing with chemicals other than water. As such, this test is appropriate for the evaluation of material performance against liquid chemicals and can be used to distinguish adequate chemical resistance for specific chemicals. This testing easily accommodates microporous and continuous film-based materials.

- Vapor transmission tests can be used for chemical vapor or gas challenges only for measuring gross vapor penetration or permeation over relatively long periods of time. Measurement of vapor transmission rates applies to any film-based materials, although some tests only apply to homogeneous films. Adsorbentbased textile fabrics or films can also be tested using this technique.

- Chemical permeation testing provides an assessment of a barrier material's total chemical resistance, permitting the measurement of relatively small amounts of permeating chemical. This test is best suited when only extremely small levels of chemical are permitted to pass through a material. Permeation testing should be employed for any type of continuous barrier material.

In the protective apparel industry, the decision to apply permeation or penetration data therefore requires a careful review of:

- The hazards associated with the chemical

- The intended duration of exposure

- The work environment

There are many cases where materials that resist liquid penetration are suitable for working environments, particularly when chemical exposure is unlikely and there is relative little hazard from wearer contact with chemical vapors. Some sample situations include working with dilute acids and bases. Having both penetration and permeation data for specific clothing products and chemicals in combination with a thorough knowledge of the chemical hazards and working environments allows the safety specialist to choose protective clothing that provides the needed level of performance. Table 15 provides sample data for three different materials including a microporous laminate. This testing illustrates how dissimilar materials can provide significantly different performance against a standard set of chemicals.

A strategy for testing a product will typically involve choosing the test method and establishing the specific conditions for the test. Many barrier tests are conducted under room temperature and humidity. Vapor transmission and permeation tests are very sensitive to these conditions, requiring a controlled environment for testing. In most cases, the duration of the test is set by the procedure, but degradation and permeation testing periods are not always specified. For these tests, test duration should be set to the maximum period of expected product use and chemical exposure. No studies have established conditions where accelerated testing provides good correlation to full-duration testing.

Test materials may also be subjected to various preconditioned prior to testing, especially for barrier testing. Preconditions may involve certain exposures intended to simulate product use such as abrasion, flexing, cleaning, or heat aging. Use of preconditioning may help to identify product barrier performance more consistent with use expectations.

Table 15 Comparison of Penetration and Permeation Resistance for Representative Liquid Splash-Protective Barrier Materials

	PVC/nylon			Saranex/Tyvek laminate			Microporous film/ nonwoven laminate		
Chemical	F903(C) Result	F739 B.T.	F739 P.R.	F903(C) Result	F739 B.T.	F739 P.R.	F903(C) Result	F739 B.T.	F739 P.R.
Acetone	Pass	8	>50	Pass	28	3.4	Pass	<4	>50
Acetonitrile	Pass	12	25	Pass	88	0.27	Pass	<4	>50
Carbon disulfide	Fail (6)	4	>50	Pass	4	>50	Pass	<4	>50
Dichloromethane	Fail (6)	4	>50	Pass	4	>50	Pass	<4	>50
Diethylamine	Fail (20)	8	>50	Pass	20	20	Pass	<4	>50
Dimethylformamide	Fail (40)	28	>50	Pass	72	1.8	Pass	<4	>50
Ethyl acetate	Pass	8	>50	Pass	20	1.5	Pass	<4	>50
Hexane	Fail (40)	20	8	Pass	None	N/A	Pass	<4	>50
Methanol	Fail (55)	16	13	Pass	None	N/A	Pass	<4	>50
Nitrobenzene	Pass	32	50	Pass	120	6.0	Pass	<4	>50
Sodium hydroxide	Pass	None	N/A	Pass	None	N/A	Pass	<4	>50
Sulfuric acid	Pass	120	6	Pass	None	N/A	Pass	<4	>50
Tetrachlorethylene	Fail (30)	16	>50	Pass	128	1.3	Pass	<4	>50
Tetrahydrofuran	Pass	8	>50	Pass	4	>50	Pass	<4	>50
Toluene	Fail (25)	12	50	Pass	24	40	Pass	<4	>50

Note: B.T., breakthrough time in minutes; P.R., permeation rate in µg/cm^2 min; N/A, not applicable. Penetration results provided as pass or fail with penetration in parentheses; permeation tests per ASTM F739 at ambient temperature for 3 h.
Source: Ref. 25.

B—
Selection of Test Chemicals

Manufacturers may be faced with a myriad of chemicals to select for testing their products. If the products are intended for broad applications among several markets, these decisions become increasingly difficult. In the past, end users in some industries were unable to compare product performance, since all manufacturers tested their materials with different sets of chemicals. The ASTM F-23 Committee sought to overcome this problem in the protective clothing industry by devising a standard battery of chemicals that represented the following [76]:

- A wide range of chemical classes

- High volume usage in the chemical industry

- Varying levels of toxicity

- Aggressive interactions with most materials

The result was a 15-liquid-chemical battery established in ASTM Standard Guide F 1001 during 1986. This battery was expanded in 1989 to include six gases as well. The standard guide permits testing groups to test either the liquid battery, gas battery, or both, as applicable. These chemicals and relevant properties are listed in Table 16. Spence [77] developed procedures that permit simultaneous permeation testing with the 13 liquid organic chemicals in the battery as a means of quickly screening material performance.

VI—
Conclusions

Various chemical barrier tests are available for establishing the performance of textile and related materials against specific chemicals. Of the three different chemical resistance approaches available, only penetration and permeation testing provide an assessment of the material's barrier performance in preventing the passage of chemical through the material. Degradation testing, while useful for examining chemical effects on materials, cannot provide information that assures barrier performance of materials. Penetration testing is usually qualitative, and the test conditions must be tailored to emulate the expected exposure conditions for discriminating material performance. While penetration testing is suitable for establishing the liquid barrier of materials, it takes consistency in operator interpretations and techniques to obtain precision in test results. It is also important to distinguish between tests that evaluate liquid repellency and those that measure liquid penetration as a result of applied pressure. Permeation testing provides the most rigorous of all chemical resistance test methods, and several techniques are available to provide flexibility in test conditions and applications. Permeation testing is suitable for establishing the vapor-barrier performance of materials. Taken collectively, the test methods described in this chapter provide a number of tools to characterize the barrier performance of materials. As with any testing, the

Table 16 ASTM F1001 Chemicals and Key Properties

Chemical	Class	Molecular weight	Vapor pressure (mm Hg)	Molar volume (cm3/mol)	Specific gravity	TLV (ppm)[*]
Acetone	Ketone	58	266	74.0	0.791	750
Acetonitrile	Nitrile	41	73	53.0	0.787	40
Ammonia	Inorganic gas	17	>760	—	N/A	25
1,3-Butadiene	Alkene	54	910	87.0	N/A	10, cancer
Carbon disulfide	Sulfur compound	76	300	62.0	1.260	10, skin
Chlorine	Inorganic gas	70	>760	—	N/A	0.5
Dichloromethane	Halogen compound	85	350	63.9	1.336	50, cancer
Dimethylformamide	Amide	73	2.7	77.0	0.949	10, skin
Ethyl acetate	Ester	88	76	99.0	0.920	400
Ethylene oxide	Heterocyclic	44	>760	—	N/A	1, cancer
Hexane	Aliphatic	86	124	131.6	0.659	50
Hydrogen chloride	Inorganic gas	37	>760	—	N/A	5
Methanol	Alcohol	32	97	41.0	1.329	200, skin
Methyl chloride	Halogen compound	51	>760	—	N/A	50, skin
Nitrobenzene	Nitro compound	123	<<1	102.7	1.203	1, skin
Sodium hydroxide	Inorganic base	40	≈0	N/A	2.130	2 mg/m^3
Sulfuric acid	Inorganic acid	98	<0.001	N/A	1.841	1 mg/m^3
Tetrachloroethylene	Halogen compound	166	14	101.1	1.631	25, cancer
Tetrahydrofuran	Ether	72	145	81.7	0.888	200
Toluene	Aromatic	92	22	106.8	0.866	50, skin

[*] Threshold Limit Value (TLV): maximum concentration of chemical permitted in air for 8 hour exposure without toxic health effects.

careful selection of the test and its parameters depends mostly on the understanding of the test product (or material) and its application.

Appendix A—
Referenced Editions of Standard Test Methods

American Association of Textile Chemist and Colorist (AATCC) Test Methods

AATCC 42, Water Resistance: Impact Penetration Test, 1989

AATCC 118, Oil Repellency: Hydrocarbon Resistance Test, 1989

AATCC 127, Water Resistance: Hydrostatic Pressure Test, 1989

American Society for Testing and Materials (ASTM) Test Methods

ASTM D471, Test Method for Rubber Property—Effect of Liquids, 1991

ASTM D543, Test Method for Resistance of Plastics to Chemical Reagents, 1987

ASTM D751, Methods for Testing Coated Fabrics, 1989

ASTM D814, Test Method for Rubber Property—Vapor Transmission of Volatile Liquids, 1991

ASTM D1003, Test Method for Haze and Luminous Transmission of Transparent Plastics, 1992

ASTM D1434, Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting, 1992

ASTM D1683, Test Method for Failure of Sewn Seams of Woven Fabrics, 1990

ASTM D1975, Practice for Environmental Stress Crack Resistance of Plastic Injection-Molded Open-Head Pails, 1991

ASTM D2062, Test Methods for Operability of Zippers, 1992

ASTM D2240, Test Method for Rubber Property—Durometer Hardness, 1991

ASTM D3132, Test Method for Solubility Range of Resins and Polymers, 1990

ASTM D3393, Specification for Coated Fabrics—Waterproofness, 1991

ASTM D3985, Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor, 1988

ASTM E96, Test Methods for Water Transmission of Materials, 1994

ASTM F88, Test Methods for Seal Strength of Flexible Barrier Materials, 1985

ASTM F739, Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids and Gases Under Conditions of Continuous Contact, 1991

ASTM F903, Resistance of Protective Clothing Materials to Penetration by Liquids, 1995

ASTM F1001, Guide for Selection of Liquid and Gaseous Chemicals to Evaluate Protective Clothing Materials, 1993

ASTM F1194, Guide for Documenting the Results of Chemical Permeation Testing on Protective Clothing Materials, 1994

ASTM F1383, Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids and Gases Under Conditions of Intermittent Contact, 1992

ASTM F1407, Test Method for Resistance of Chemical Protective Materials to Liquid Permeation—Permeation Cup Method, 1992

European Community (CEN) Test Methods

EN 368, Protective clothing—Protection against liquid chemicals—Test Method: Resistance of materials to penetration by liquids, 1992

EN 369, Protective clothing—Protection against liquid chemicals—Test method: Resistance of materials to permeation by liquids, 1993

EN 374-3, Protective gloves against chemicals and microorganisms—Part 3: Determination of resistance to permeation by chemicals, 1994

International Standards Organization (ISO) Test Methods

ISO 2556, Plastics—Determination of the gas transmission rate of films and thin sheets under atmospheric pressure—Manometric method, 1974

ISO 6529, Protective clothing—Protection against liquid chemicals—Determination of resistance of air-impermeable materials to permeation of liquids, 1990

ISO 6530, Protective clothing—Protection against liquid chemicals—Determination of resistance of materials to penetration by liquids, 1990

ISO 8096, Rubber- or plastics coated fabrics water-resistant clothing—Specification—Part 1: PVC-coated fabrics; Part 2: Polyurethane- and silicone elastomer-coated fabrics, 1989

U.S. Federal Government Test Methods (FTMS)

FTMS 191A,5512—Water Resistance of Coated Cloth; High Range, Hydrostatic Pressure Method, 1990

FTMS 191A,5514—Water Resistance of Coated Cloth; Low Range, Hydrostatic Pressure Method, 1990

FTMS 191A,5516—Water Resistance of Cloth; Water Permeability. Hydrostatic Pressure Method, 1990

FTMS 191A,5520—Water Resistance of Cloth; Drop Penetration Method, 1990

FTMS 191A,5522—Water Resistance of Cloth: Water Impact Penetration Method, 1990

FTMS 191A,5524—Water Resistance of Cloth; Rain Penetration Method, 1990

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