Correlation Between Limiting Oxygen Index and Phosphorus/Nitrogen Content of Cotton Fabrics Treated with a Hydroxy-Functional Organophosphorus Flame-Retarding Agent and Dimethyloldihydroxyethyleneurea

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ABSTRACT: The combination of a hydroxyl-functional organophosphorus flame-retarding agent (FR) and dimethyloldihydroxyethyleneurea (DMDHEU) was used as a durable flame-retardant finish system for cotton fabrics. DMDHEU functions as a binder between FR and cotton cellulose, thus making this flame-retarding system durable to home laundering. DMDHEU also provides nitrogen to this system, therefore enhances its performance. Limiting oxygen index (LOI) is one of the most commonly used parameters to indicate the flammability of textiles and other polymeric materials. In this research, we investigated the correlation between LOI and phosphorus/nitrogen content on the cotton fabric treated with that durable flame-retardant system. Phosphorus concentration on the fabric was analyzed by inductively coupled plasma atomic emission spectroscopy, whereas the nitrogen content was determined indirectly by measuring the carbonyl band intensity in the infrared spectra of the treated fabric. We developed a statistical model to predict LOI of the cotton fabric treated with FR and DMDHEU based on the phosphorus concentration and the intensity of carbonyl band of DMDHEU on cotton.
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Key words: cotton; dimethyloldihydroxyethyleneurea; flame-retardant finishing; organophosphorus chemicals; limiting oxygen index; infrared spectroscopy

INTRODUCTION

Durable flame-retardant finishes for cotton commonly used by the industry include the tetrakis(hydroxymethyl)phosphonium chloride-based system and reactive organophosphorus chemicals.[1–3] However, several limitations are associated with those flame retardant finishing systems,[4] thus making it urgent to develop effective durable flame retardant systems for cotton.

N-methylol reagents, such as dimethyloldihydroxyethyleneurea (DMDHEU), have long been used in the textile industry as crosslinking agents for cotton to produce wrinkle-resistant cotton fabric.[5] Hydroxy-functional organophosphorus compounds (FR), such as the one shown in Scheme 1, where X and Y are alkoxyl and alkyl groups,[6] can be used as a durable flame-retardant finishing agents for cotton when DMDHEU is present as a crosslinking agent.

The use of the oxygen index method for evaluating the flammability of plastics and textiles started in 1966.[7] Since then the oxygen index, often called limiting oxygen index (LOI), has been used extensively in the academic community as well as in industry, and it continues to be widely used today in evaluation of flame-retardant materials.[8] LOI is defined as the minimum percentage of oxygen that allows a sample to sustain combustion under specified conditions in a candle-like fashion.[2] A number of researchers have showed the correlation between LOI and results of other testing methods.[9–15]

The LOI test is easy to run and usually reproducible, but it is also time-consuming. Determining phosphorus content and carbonyl band intensity using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Fourier transform infrared spectroscopy is fast, efficient, and requires a much smaller sample size. In this research, we investigated the correlation between LOI and the phosphorus/nitrogen contents on the cotton fabric treated with the durable flame-retarding system, and developed a statistical model to predict LOI-based phosphorus/nitrogen content of the treated cotton fabric.

EXPERIMENTAL

Materials

The fabric used was a desized, scoured, and bleached 40×40 cotton printcloth weighing 108 g/m^2 (Testfab-

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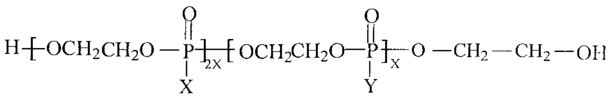
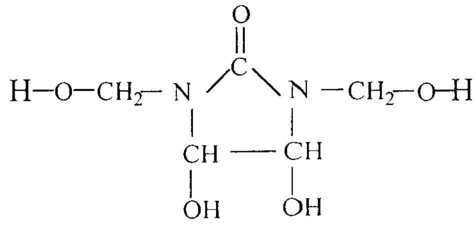


Scheme 1



Scheme 2

ric Style 400). The hydroxy-functional organophosphorus oligomer was supplied by Akzo Nobel Chemical Corporation, Dobbs Ferry, New York. DMDHEU ("Freerez 900") and the catalyst ("Catalyst 531") were supplied by Noveon, Cleveland, Ohio, and OMNOVA Solution, Chester, South Carolina, respectively.

Fabric treatment and home laundering washing/drying procedures

The cotton fabric was first immersed in a finish solution containing FR, DMDHEU, and the catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and then cured in a Mathis curing oven at a specified temperature. All the concentrations presented here are based on weight of bath (w/w, %). The wet pick-up of the cotton fabric was approximately 115±2%. After curing, the treated cotton fabric was subjected to one home laundering washing/drying cycle without the use of a detergent (specified here as "water wash") to remove the chemicals not bound to the fabric. The home laundering wash/dry (HLWD) process was done using a standard detergent ("AATCC Detergent 1993") according to AATCC Test Method 124-1996. The water temperature was approximately 46°C.

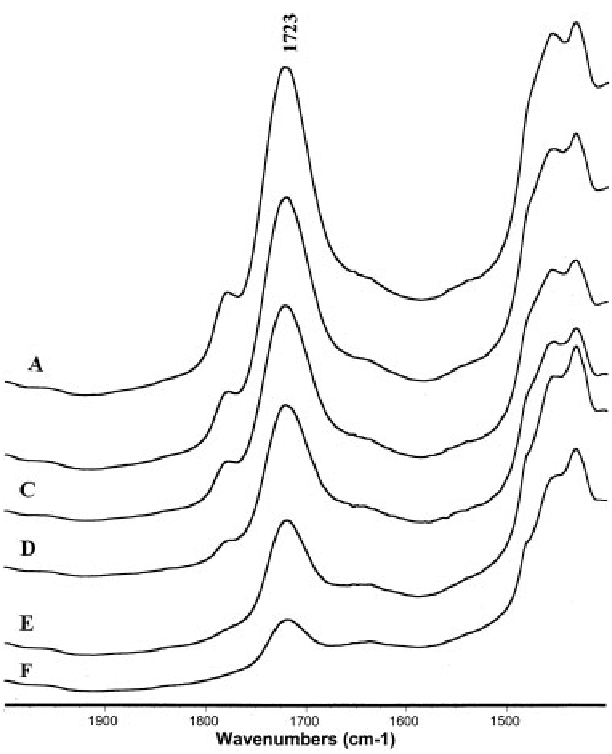


Figure 1 Diffuse reflectance infrared spectra of the cotton fabric treated with 24% FR and DMDHEU of different concentrations (a–f): 12, 10, 8, 4, 2, and 1%.

LOI measurement

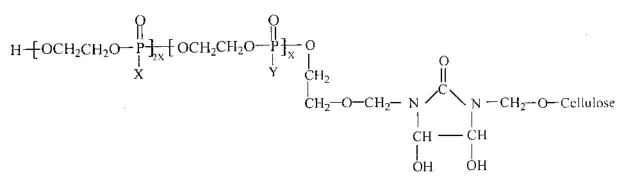
LOI of the treated cotton fabric was measured according to ASTM Standard Method D2863-97.

Determination of phosphorus concentration on the treated cotton fabric

Approximately 2 g of the treated cotton fabric taken from different parts of a larger fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. Two milliliters of concentrated H_2SO_4 was added to 0.1 g of cotton powder. Ten milliliters of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until dense SO_3 vapor is produced. The completely digested cotton sample as a clear solution was transferred to a 50-mL volumetric flask, then diluted with distilled/deionized water. The sample thus prepared was analyzed using a Thermo-Farrell-Ash Model 965 ICP/AES instrument to determine the percent concentration of phosphorus.

Infrared spectroscopy measurement

All the infrared spectroscopy data presented here are diffuse reflectance spectra and are presented in absorbance mode ($-\log R/R_0$). Resolution for all the infrared spectra is 4 cm^{-1}, and there were 120 scans for each spectrum. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. To measure the carbonyl band intensity, the treated and cured cotton fabric was



Scheme 3

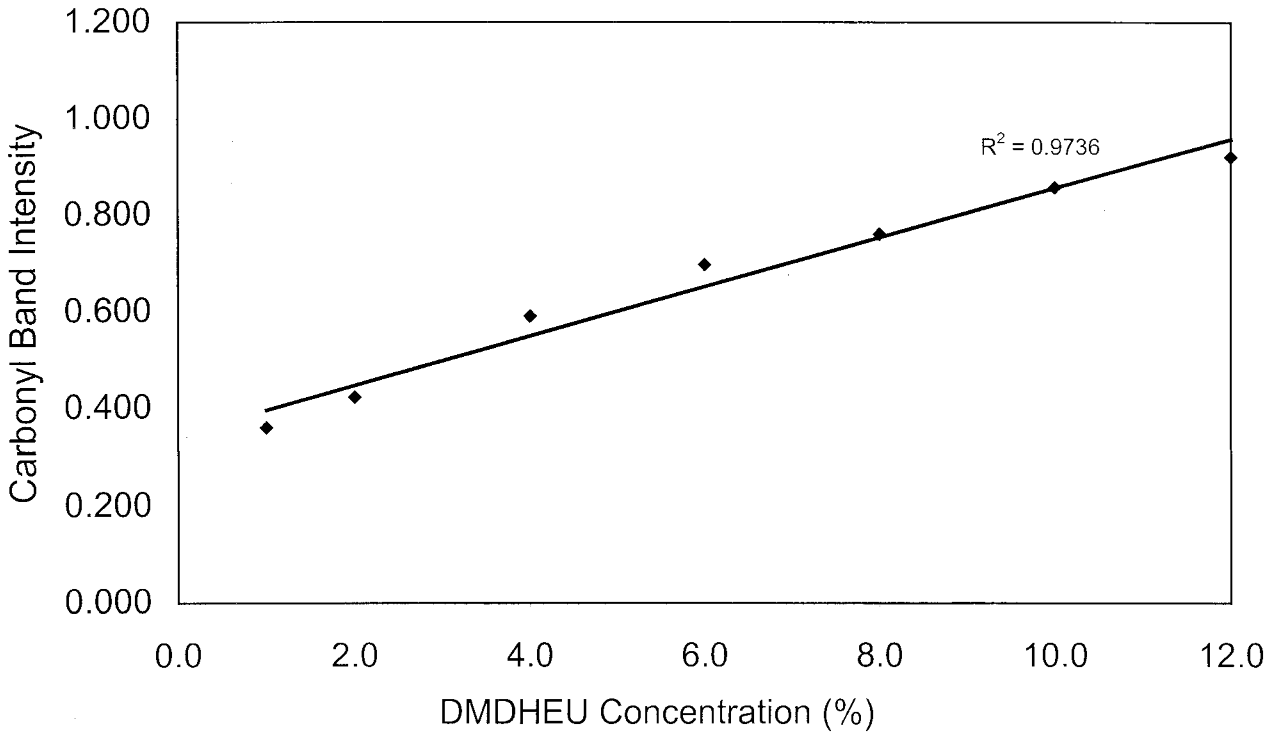


Figure 2 The carbonyl band intensity of the fabric treated with 24% FR and different concentrations of DMDHEU, and cured at 165°C for 2.5 min as a function of DMDHEU concentration.

first washed in water to remove the FR and DMDHEU not bound to cotton and the catalyst, then dried at 80°C for 5 min. To improve sample uniformity, a fabric sample was ground in a Wiley mill to form a powder before infrared spectroscopy analysis. The carbonyl band intensity in the infrared spectra was normalized against the 1318 cm^{-1} band associated with a C—H bending mode of cellulose.

RESULTS AND DISCUSSION

The cotton fabric was treated with 24% FR in combination of DMDHEU with concentration ranging from 1 to 12%, then cured at 165°C for 2.5 min. The infrared spectra of the cotton fabric thus treated are presented in Figure 1, in which the band at 1723 cm^{-1} is due to the carbonyl stretching mode of DMDHEU (Scheme 2). The intensity of carbonyl band increases as the DMEHEU concentration of the solution increases. The carbonyl band intensity is plotted against the DMDHEU concentration in the solution (Fig. 2). One observes a linear relationship between the carbonyl band intensity of the treated fabric and the DMDHEU concentration in the solution (Fig. 2). Since the carbonyl band intensity is proportional to the quantity of DMDHEU, the carbonyl band intensity can be used as an indirect measure of the nitrogen content on the fabric due to DMDHEU bound to the fabric.

DMDHEU has four hemi-acetal groups to react with the hydroxyl groups of cellulose as well as ones of FR.

TABLE I
LOI, Carbonyl Band Intensity, and Phosphorus Concentration of the Cotton Fabric Treated with 24% FR and DMDHEU of Different Concentrations, and Cured at 165°C for 2.5 min

	LOI (%)				Carbonyl band intensity				Phosphorus (%)			
DMDHEU (%, ow[a])	Before wash	1 HLWD	5 HLWD	10 HLWD	Before wash	1 HLWD	5 HLWD	10 HLWD	Before wash	1 HLWD	5 HLWD	10 HLWD
1	29.2	25.4	23.3	21.2	0.306	0.270	0.249	0.233	3.42	1.58	1.01	0.65
2	29.5	27.6	26.3	23.5	0.428	0.423	0.393	0.345	3.72	2.22	1.82	1.03
4	31.0	29.1	28.8	28.0	0.631	0.628	0.626	0.546	3.92	2.84	2.55	2.35
6	31.3	29.0	28.9	28.2	0.699	0.697	0.690	0.680	3.97	3.22	2.89	2.59
8	30.6	29.2	28.9	28.3	0.871	0.843	0.839	0.821	4.02	3.25	2.92	2.65
10	31.6	29.8	29.6	29.4	0.872	0.856	0.866	0.841	4.08	3.28	3.02	2.90
12	31.6	29.8	29.6	29.5	0.934	0.920	0.917	0.908	4.10	3.34	3.02	3.00

[a]ow, weight of both.

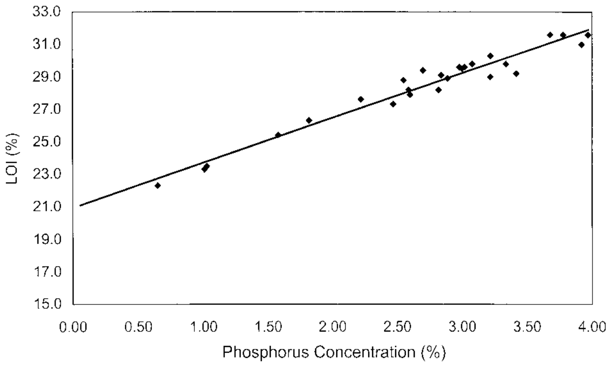


Figure 3 LOI of the fabric treated with 24% FR and DMDHEU of different concentration, cured at 165°C for 2.5 min, and after different HLWD cycles, as a function of phosphorus concentration on the fabric.

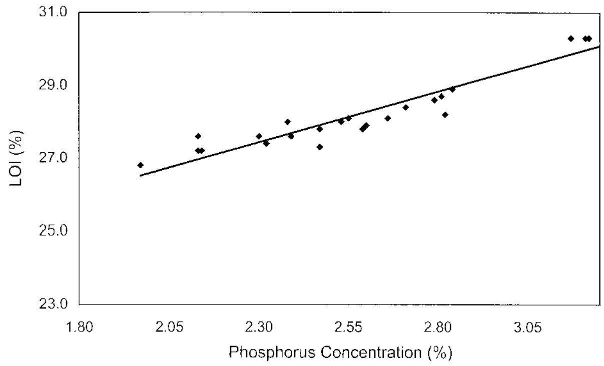


Figure 4 LOI of the fabric treated with 24%FR/8%DMDHEU, cured at different temperatures for 2.5 min, and subjected to different numbers of home laundering cycles as a function of phosphorus concentration on the fabric.

Among the four groups, the two hemi-acetal groups derived from formaldehyde are significantly more reactive than those derived from glyoxyl. DMDHEU functions as a binder between FR and cotton fabric (Scheme 3), thus making this flame-retardant finishing system a durable one. DMDHEU also provides nitrogen to this system, and therefore enhances performance of this flame retardant system due to phosphorus/nitrogen synergism.

The cotton fabric was treated with 24% FR and DMDHEU of different concentrations, cured at 165°C for 2.5 min. The LOI, carbonyl band intensity, and phosphorus concentration of treated fabrics are shown in Table I. LOI and carbonyl band intensity increase as the concentration of DMDHEU increases. As the concentration of DMDHEU increases from 1 to 12%, one observes that the phosphorus content of the treated fabric remains practically unchanged, whereas the LOI value (before wash) increases from 29.5 to 31.6 (Table I). The data indicate that DMDHEU provides phosphorus/nitrogen synergism to the flame-retarding system, thus improving the flame-retardant performance of the treated fabric.

The treated cotton fabric was also subjected to different number of HLWD cycles. At each DMDHEU concentration level, the higher the number of home laundering cycles, the lower the phosphorus content and LOI value for the treated fabric become. LOI values of the cotton fabric treated with 24% FR and DMDHEU of different concentrations is plotted against the phosphorus content on the treated fabric (Fig. 3), in which a linear correlation exists between LOI and the phosphorus content of the treated fabric.

The cotton fabric was treated with 24% FR and 8% DMDHEU, and cured at different temperatures for 2.5 min. The treated and cured fabric were also subjected to different numbers of HLWD cycles. The LOI, carbonyl band intensity, and phosphorus content of the cotton fabric cured at different temperatures are presented in Table II. LOI is plotted against the phosphorus content of the treated fabric (Fig. 4). Once again, the data show a good linear relationship between LOI value and the phosphorus content of the fabric.

The cotton fabric was treated with FR/DMDHEU of different concentrations with a constant FR-to-DMDHEU ratio of 3:1 and cured at 165°C for 2.5 min. The treated cotton fabric was then subjected to different number of HLWD cycles. The LOI, carbonyl band intensity, and phosphorus content of the fabric is presented in Table III. LOI, carbonyl band intensity, and

TABLE II
LOI, Carbonyl Band Intensity, and Phosphorus Concentration of the Cotton Fabric treated with 24% FR and 8% DMDHEU, and Cured at Different temperature for 2.5 min

Curing temp. (°C)	LOI (%)				Carbonyl band intensity				Phosphorus (%)			
	Before wash	1 HLWD	5 HLWD	10 HLWD	Before wash	1 HLWD	5 HLWD	10 HLWD	Before wash	1 HLWD	5 HLWD	10 HLWD
130	30.3	28.4	28.0	27.6	0.830	0.737	0.790	0.732	3.29	2.71	2.38	2.13
140	30.3	28.6	28.0	27.6	0.803	0.791	0.802	0.801	3.22	2.79	2.53	2.30
150	30.3	28.7	28.1	27.6	0.827	0.784	0.813	0.800	3.28	2.81	2.66	2.39
160	30.3	28.9	28.1	27.4	0.870	0.810	0.824	0.805	3.34	2.84	2.55	2.32
165	30.3	28.2	27.9	27.3	0.871	0.843	0.839	0.821	3.22	2.82	2.60	2.47
170	30.3	27.3	27.8	27.2	0.837	0.800	0.848	0.794	3.21	2.74	2.59	2.14
180	30.3	27.8	27.2	26.8	0.913	0.862	0.845	0.825	3.17	2.47	2.13	1.97

TABLE III
LOI, Carbonyl Band Intensity, and Phosphorus Concentration of the Cotton Fabric Treated with FR/DMDHEU (3:1) of Different Concentrations, Cured at 165°C for 2.5 min

FR conc. (%)	LOI (%)				Carbonyl band intensity				Phosphorus (%)			
	Before wash	1 HLWD	5 HLWD	10 HLWD	Before wash	1 HLWD	5 HLWD	10 HLWD	Before wash	1 HLWD	5 HLWD	10 HLWD
4	22.2	20.3	19.7	19.4	0.389	0.372	0.443	0.399	0.82	0.50	0.39	0.33
8	24.5	22.5	22.0	21.9	0.562	0.504	0.542	0.504	1.44	1.04	0.88	0.76
12	26.8	24.9	24.7	24.2	0.655	0.638	0.616	0.596	2.09	1.57	1.39	1.27
16	28.5	26.9	26.7	26.5	0.742	0.709	0.684	0.676	2.62	2.13	1.85	1.92
18	29.6	27.7	27.7	27.6	0.781	0.730	0.713	0.691	2.83	2.33	2.16	2.08
20	30.0	28.8	28.5	27.9	0.787	0.748	0.753	0.729	3.01	2.44	2.33	2.13
24	30.3	28.2	27.9	27.3	0.871	0.843	0.839	0.821	3.22	2.82	2.60	2.47

phosphorus content of the treated fabric increase as the concentration of FR/DMDHEU increases, and decrease as the number of laundering increases. At each FR/DMDHEU concentration level, a larger number of laundering cycles results in lower phosphorus content and lower LOI value of fabrics. As the concentration of FR increased from 4 to 24%, the LOI after 10 HLWD increased from 19.4 to 27.3. LOI is plotted against the phosphorus content of the treated fabric (Fig. 5).

All LOI values, phosphorus contents, and carbonyl band intensities of the treated fabric were used as the basis to develop a statistical model. We used the SAS program to develop a least square estimated regression function between LOI value and the phosphorus content/carbonyl band intensity, shown in eq. (1) and Table IV, where Y refers to the LOI value, X_1% refers to the phosphorus content, and X_2% refers to the carbonyl band intensity of the fabric.

$$Y(\%) = 18.54 + 2.87X_1\% + 2.83X_2\% \qquad (1)$$

Equation (1) gives an R^2 of 0.9567 (Table V), thus indicating that more than 95% of the total variability of LOI is associated with the variability of the independent variables (phosphorus content and carbonyl band intensity) within the framework of the equation. To achieve an appropriate linear regression model, $Y = \beta_0 + \beta_1 X_1 + \cdots \beta_n X_n + \epsilon_i$, it is necessary to make the following assumptions on the residuals ϵ_i: (1) $\epsilon_1, \epsilon_2, \cdots \epsilon_n$ are independent; (2) $\epsilon_1, \epsilon_2, \cdots \epsilon_n$ have a identical distribution; and (3) $\epsilon_1, \epsilon_2, \cdots \epsilon_n$ have a normal distribution, with mean 0 and variance σ^2.[16]

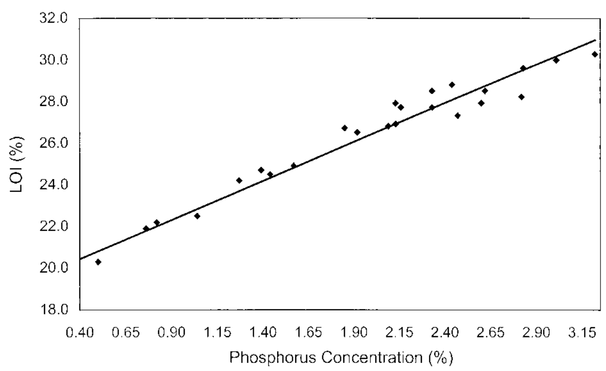


Figure 5 LOI of the fabric treated with different FR/DMDHEU (3:1) concentrations, cured at 165°C for 2.5 min, and subjected to different numbers of home laundering cycles as a function of phosphorus concentration on the fabric.

The diagnostic plots of residuals, such as the one presented in Figure 6, show that all the residuals fall within a horizontal band centered around 0, displaying no systematic tendencies, meaning that all the residuals are random, and the linear regression is appropriate.

From the Shapiro–Wilk W normality test,[16] W is 0.977543, and p value is 0.2324 (Table VI). Both W and p values are large, meaning the residuals come from normal distribution.

Test of the overall hypothesis shows that F value is 873.51 and P value is <0.0001, meaning that we can accept the alternative hypothesis (Ha), that at least one of the β's is not equal to zero (Table V). The statistical analysis shows that LOI value does depend on all predictor variables: phosphorus content and carbonyl band intensity. The phosphorus content and carbonyl band intensity are the two significant factors for determining the flammability of the fabric. From the diagnostics of the regression model, we conclude that the linear least square estimated regression function between LOI and phosphorus content and carbonyl band intensity is appropriate, meaningful, and useful.

TABLE IV
Parameter Estimates for Cotton Fabric Treated with FR/DMDHEU

Variable	*DF*	Parameter estimate	Standard error	*t* value	*Pr* > | t |
Intercept	1	18.54531	0.24796	74.78	<0.0001
X_1	1	2.87061	0.12124	23.68	<0.0001
X_2	1	2.82948	0.50820	5.57	<0.0001

TABLE V
Analysis of Variance for Cotton Fabrics Treated with FR/DMDHEU[a]

Source	*DF*	Sum of square	Mean square	*F* value	$Pr > F$
Model	2	818.64285	409.32142	873.51	<0.0001
Error	79	37.01911	0.46860		
Corrected total	81	855.66195			

[a] $R^2 = 0.9567$; adjusted $R^2 = 0.9556$.

CONCLUSIONS

When the combination of a hydroxy-functional organophosphorus flame-retarding agent and DMDHEU are used as a durable flame-retardant finish system for cotton, a linear least square estimated regression function exists between the LOI and phosphorus content/carbonyl band intensity. The carbonyl band intensity is used as an indirect measure of the nitrogen content on fabrics due to DMDHEU bound to cotton. Analysis of regression shows that this is an appropriate and meaningful regression model. The model can be used to predict LOI of treated fabrics based on the phosphorus concentration and nitrogen concentration indirectly measured using the intensity of carbonyl band of DMDHEU in the infrared spectra of the treated fabrics.

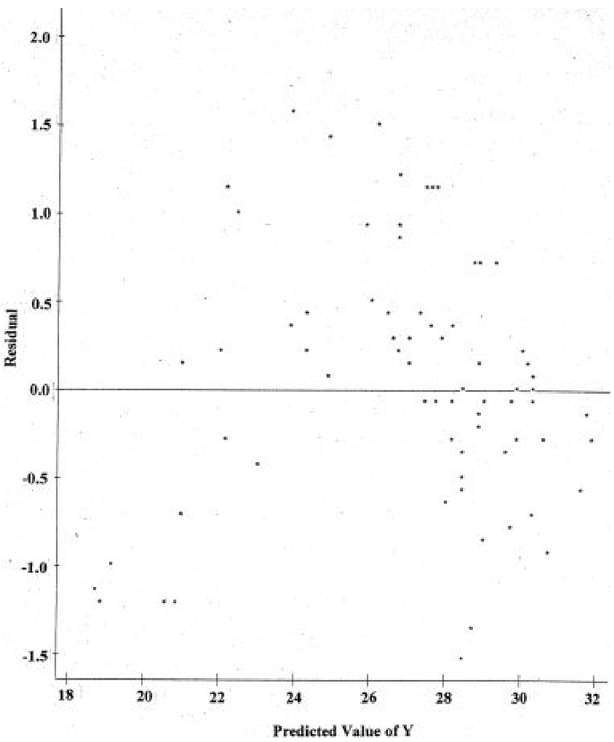


Figure 6 Plot of the residual vs predicted value of Y (LOI).

TABLE VI
Normality Tests for Cotton Fabrics Treated with FR/DMDHEU

Test	Statistic	*P* value
Shapiro–Wilk	W 0.980081	$Pr < W$ 0.2324
Kolmogorov–Smirnov	D 0.07045	$Pr < D > 0.1500$
Cramer–von Mises	W^2 0.068122	$Pr < W^2 > 0.2500$
Anderson–Darling	A^2 0.463778	$Pr < A^2 > 0.2500$

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