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# Effect of Phthalonitrile and Alum on Flame Retardation Properties of 100% Cotton Fabric

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**Abstract**

Speculations have it that phthalonitrile imparts flame retardancy on substrates. This study aimed to investigate the activities of phthalonitrile as flame retardant on 100% cotton fabric. The fabric samples tested were cut into $25.4 \times 7$ *cm* pieces, scoured, dried, and weighed. They were then impregnated with different concentrations of phthalonitrile in different solvents (benzene and acetone) and emulsion alongside alum dissolved in water. At the same time, the untreated fabric was used as a control. All the impregnated pieces of fabric were dried at room temperature and reweighed. The fabrics were subjected to add-on%, after flame time, after-glow time, and % char formation tests. The results showed that cotton-tested flame retardant properties increase with the increase in the concentration of phthalonitrile. Phthalonitrile has flame retardant properties on 100% cotton fabric.

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*Keywords:* Flame retardant, Phthalonitrile, Cotton fabric, Alum, Percent add-on, Flame and glow time, Char formation

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## 1. Introduction

Fire hazards associated with natural and synthetic polymeric materials cause loss of lives and property. These vast losses and property destruction concern governmental regulatory bodies, consumers, and industrial manufacturers.

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Wilson reported that according to the US Fire Administration of the Department of Homeland Security, between 1992 and 2001, an average of over 4200 people were killed by fire each year in the United States, and 25,000 were injured (excepting victims of the attacks on September 11, 2001) [1, 2]. Fire results from a chemical reaction in which heat from a combustible fuel is transferred to heat and light. The flame of a fire is the visible sign of light that occurs when gas is heated, and it is proof that a fire has occurred [3, 4]. Fire has been highlighted as the most severe threat to the safety of industrial plants and all Nigerian workplaces. A fire can cause substantial property damage and destruction, as well as injuries and death among the people of a building [5]. Even if fires do not injure workers, they can cause tremendous disruption and bring most operations to a halt. Fires can result in the destruction of property and the loss of valuable documents and information, necessitating the establishment of clear fire safety standards to reduce fire outbreaks and the loss that can occur as a result of such hazards. Nigeria ranked top in the world for fire deaths in 2016, according to the "World Life Expectancy Report" [6]. The lack of awareness of fire prevention and escape tactics is the cause, not the number of fires itself. On October 18, 1998, a pipeline exploded in the Jesse community [7]. Although the cause of the explosion is unknown, the Jesse fire is distinguished as Nigeria's deadliest pipeline disaster, with 1,082 deaths. Since then, fires have erupted in Nigerian markets and urban areas at alarming rates. Unpredictable power surges, unauthorized electrical connections, faulty electrical fittings, inadequate electrical materials, and the usage of domestic generators are among the causes of such fires [8]. Adequate fire safety management is based on enforcing fire prevention legislation that identifies all potential risks connected with specific locations and the effective assessment of the measures in place [6].

Cotton is an essential textile that contains cellulose. The fabrics hold a significant share in the textile market. It is widely used to produce apparel, home furnishings, sleepwear, and various industrial products due to cotton's excellent properties such as strength, flexibility, softness, air and water permeability, and comfortability. However, cotton fabric is highly flammable. Cotton fabric fires can cause injury (burns), deaths, and financial losses. Cotton fabric must be given flame-retardant treatment to reduce its flammability.

The phenolate salts of petroleum-based bisphenols (e.g., 4,4'-biphenol, bisphenol A, bisphenol AF, etc.) and 4-nitrophthalonitrile are used to make the first generation phthalonitrile (PN) resins, which have been intensively researched. Despite the outstanding physical qualities of the resultant polymers and composites, the PN resins have a high melting point (195–230 $^{o}C$) and a short processing window, making composite structure manufacturing problematic [8]. Because of these intrinsic processing restrictions, second-generation PN resins with oligomeric aromatic ether spacers between the terminal phthalonitrile groups were developed. They're made utilizing a two-step, one-pot nucleophilic displacement reaction involving activated or inactivated Di haloaromatic compounds and a suitable bisphenol, followed by 4-nitrophthalonitrile end-capping. The low melting temperatures of the second-generation PN resins allow them to be processed at far lower temperatures than the first-generation PN resins [9, 10]. Given the unique physical properties of PN resin, we decided to use the solution of phthalonitrile (Benzene-1,2-dicarbonitrile) to impregnate cotton fabrics to ascertain its suitability as flame retardant based on parameters such as add-on, after flame time, after-glow time, ignition time, and char formation [11].

## 2. Materials and Methods

Phthalonitrile and all reagents were of analytical grade and were purchased from Aldrich, Germany. Fire Resistance Test Cabinet was constructed according to AATCC Test Method-34, 1969, with wood and glass measuring $30.5 \times 30.5 \times 76.2\ cm$.

### 2.1. Sample preparation

All test fabrics (cotton) were cut into $(25.4 \times 7)\ cm$, weighed, and washed for 60 minutes with 3 $g/L$ soda ash and 1 $g/L$ ESUT liquid non-ionic detergent at 90 $^{o}C$ in a water bath using a liquid to fabric ratio of 1:20. The materials were rinsed once with lots of warm water followed by cold water and air-dried at room temperature for 24 hours.

### 2.2. 2.2. Treatment of 100% cotton fabric with various concentrations of phthalonitrile in different solvents and alum in water

Solutions of phthalonitrile were made by dissolving 0.5, 1.0, 1.5, and 2.0 $g$ each in 100 $mL$ benzene and acetone, respectively. Also, alum solutions were made by dissolving 0.5, 1.0, 1.5, and 2.0 $g$ of alum in 100 $mL$ water. Fabrics were impregnated in the alum solutions and left for 1 hour. Fabrics were impregnated in each emulsion for 4 hours and dried at room temperature. Afterwards, the whole fabrics were removed and spread to dry for 24 hours at room temperature.

### 2.3. Analyses of flame retardation parameter

These analyses evaluated the flame retardancy of treated cotton fabrics using the following parameters: add-on%, after flame time, after-glow time, and % char formation.

### 2.4. Determination of percent add-on

The treated cotton fabrics were weighed before and after impregnation with phthalonitrile and alum. The difference in weight of phthalonitrile and alum-impregnated cotton fabrics was used to calculate the percent add-on [12-14].

Add–on (%) was calculated using the equation:

$$Add - on(\%) = \frac{(weight\ of\ treated\ fabric) - (weight\ of\ untreated\ fabric)}{(weight\ of\ untreated\ fabric)} \times 100. \tag{1}$$

### 2.5. Determination of the after-flame time

This test evaluates the extent of retardation due to phthalonitrile and alum impregnation. The set of the impregnated and control fabrics to be tested were clamped vertically in the fire resistance test cabinet. The fabric was ignited at the base, and the glass screen closed alongside starting a stopwatch immediately. The stopwatch was stopped immediately the flame stopped. The duration of flaming (ignition time to the time the flame stopped) was read from the stopwatch and recorded in seconds.

### 2.6. Determination of percent char formation

This study investigated the extent to which the flame consumed the impregnated fabric and compared whether it turned into ash with control. The impregnated and control fabrics were weighed before burning, and the char was weighed after burning. The percent char formation was calculated by dividing the fabric weight after burning by the weight before burning multiplied by 100, as shown in equation 2 [15, 16].

$$\%Char\ Formation = \frac{(Weight\ of\ cotton\ fabric\ after\ burning)}{(Weight\ of\ cotton\ fabric\ before\ burning)} \times 100. \tag{2}$$

## 3. Results and Discussion

The add-on% of phthalonitrile dispersed in an emulsifier, dissolved in acetone, and benzene was measured against each concentration. Results revealed that add-on% increases almost linearly as concentration increases. Comparing the rate of absorption of phthalonitrile by cotton fabric, Table 1 showed that fabric absorbed more phthalonitrile dispersed in an emulsion than phthalonitrile in acetone and benzene, which are almost the same. The alum solution was prepared in water because of its comparatively low volatility and solubility, and from this, a series of concentrations were made.

The add-on% was obtained and shown in Figure 1. Also, phthalonitrile dispersed in emulsion has a better add-on% than the control (alum in water). Phthalonitrile dissolved in benzene and phthalonitrile in acetone almost had the same add-on%.

The effect of phthalonitrile dispersed in emulsion, dissolved in benzene and acetone, was compared with the control (effect of alum dissolved in water) after flame time. The two flame retardants (phthalonitrile and alum) ranged from 0 to 2.0 $g/ml$. After the flame time, cotton fabric impregnated with PN in emulsion showed a better after-flame time, followed by PN dissolved in benzene and PN dissolved in acetone. The percent flame retardation optimal was 89.7% for 2.0 $g/ml$ concentration of PN in emulsion and 62.64% for 2.0 $g/ml$ concentration of PN in benzene; the least is 23.35% for 2.0 $g/ml$ concentration of PN in acetone while the control is 43.61%. This result showed that PN in the emulsion is a better flame retardant than alum, PN in acetone, and PN in benzene (Table 2).

Table 1. Effect of phthalonitrile and alum concentration on percent add-on.

| | PN EMULSION | | | PN ACETONE | | | PN BENZENE | | | ALUM IN WATER | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | WU | WT | AO | WU | WTF | AO | WU | WT | A | WU | WT | AO |
| | F | F | | F | | | F | F | O | F | F | |
| 0 | 2.28 | 2.28 | 0 | 2.08 | 2.08 | 0 | 2.12 | 2.12 | 0 | 2.24 | 2.24 | 0 |
| 0.5 | 2.28 | 2.55 | 11.8 | 2.22 | 2.25 | 1.3 | 2.24 | 2.28 | 1.7 | 2.23 | 2.31 | 3.5 |
| 1.0 | 2.28 | 2.57 | 12.7 | 2.16 | 2.22 | 2.7 | 2.21 | 2.29 | 3.6 | 2.12 | 2.23 | 5.1 |
| 1.5 | 2.28 | 2.67 | 17.1 | 2.12 | 2.23 | 5.18 | 2.18 | 2.31 | 5.9 | 2.15 | 2.31 | 7.4 |
| 2.0 | 2.28 | 2.75 | 20.6 | 2.23 | 6.27 | 6.27 | 2.21 | 2.38 | 7.6 | 2.08 | 2.29 | 10.1 |

C – CONCENTRATION (g/mL); WUF – Weight of untreated fabric (g); WTF - Weight of treated fabric (g); AO – Add-on (%)

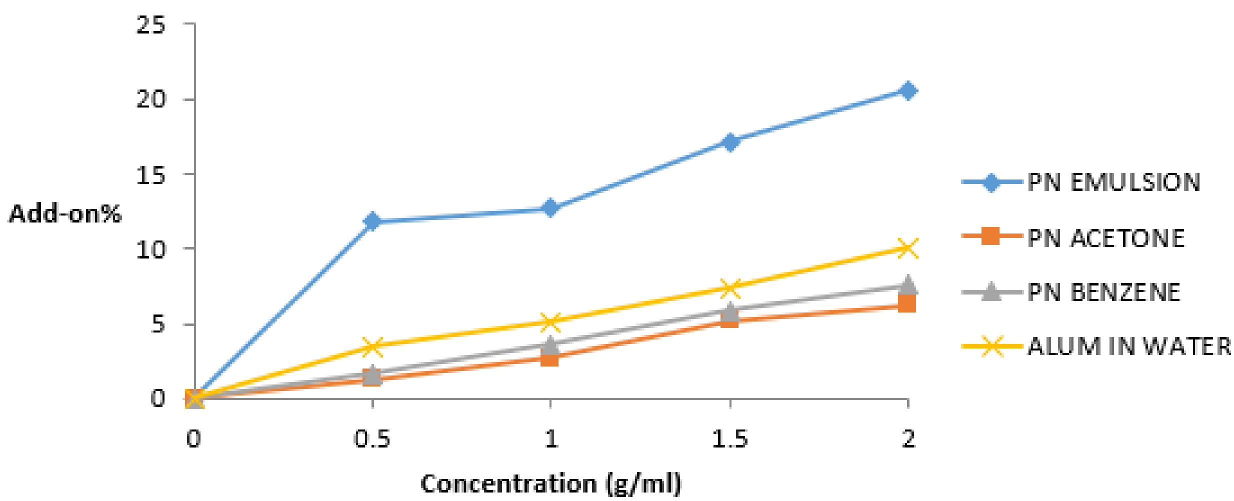


Figure 1. Effect of phthalonitrile/alum concentration on add-on%.

Table 2. Effect of phthalonitrile and alum concentration after flame time

| Conc. | Fab. | PN in Emulsion | | PN in Acetone | | PN in Benzene | | Alum in Water | |
|---|---|---|---|---|---|---|---|---|---|
| (g/mL) | Length(cm) | AFT(s) | Reta(%) | AFT(s) | Reta(%) | AFT(s) | Reta(%) | AFT(s) | Reta(%) |
| 0 | 25.4 | 17.13 | 0 | 17.13 | 0 | 17.13 | 0 | 17.13 | 0 |
| 0.5 | 25.4 | 25.00 | 45.90 | 18.70 | 9.17 | 20.73 | 21.0 | 21.10 | 23.18 |
| 1.0 | 25.4 | 29.20 | 70.40 | 19.63 | 14.59 | 24.13 | 40.86 | 22.80 | 33.10 |
| 1.5 | 25.4 | 30.90 | 80.30 | 20.63 | 20.43 | 26.06 | 52.13 | 23.40 | 36.60 |
| 2.0 | 25.4 | 32.50 | 89.70 | 21.13 | 23.35 | 27.86 | 62.64 | 24.60 | 43.61 |

The percent flame retardation of the cotton fabric, as shown in Figure 2, varies directly with PN concentration. That is, an increase in the concentration of flame retardant increases percent retardation.

The effect of phthalonitrile concentration dispersed in emulsion, phthalonitrile dissolved in acetone, PN in benzene, and alum in water on after-glow time indicated that after-glow time decreases as the concentration of the flame retardants increases. From Figure 3, AGT of cotton fabric impregnated with alum in water showed the best AGT of 41.40 *seconds* at 2.0 $g/ml$, followed by the AGT of phthalonitrile dispersed in emulsion and AGT of phthalonitrile in benzene of 54.4 and 55.20 *seconds* respectively while the least took 57.80 *seconds* to glow and that is phthalonitrile in acetone (Table 3). Glow is a heterogeneous oxidative surface reaction that depends on the nature of burnt material and the oxygen available [17-19].

The % char formation of phthalonitrile dispersed in emulsion, dissolved in acetone, dissolved in benzene, and alum

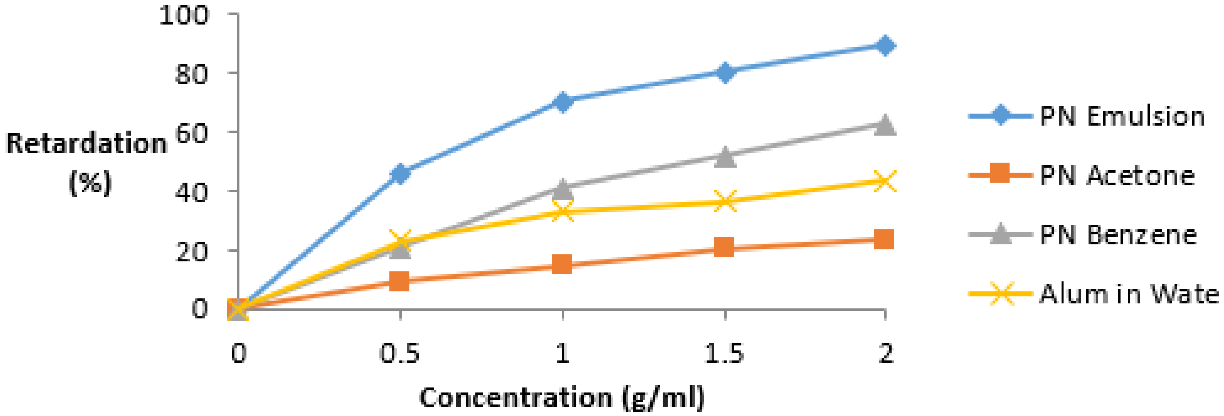


Figure 2. Effect of phthalonitrile and alum concentration after flame time.

Table 3. Effect of phthalonitrile and alum concentration on after-glow time

| Conc. (g/ml) | Fab. Length (cm) | PN in Emulsion AGT(s) | PN in Acetone AGT(s) | PN in Benzene AGT(s) | Alum in Water AGT(s) |
|---|---|---|---|---|---|
| 0 | 25.4 | 76.26 | 76.26 | 76.26 | 76.26 |
| 0.5 | 25.4 | 66.4 | 75.8 | 69.53 | 68.20 |
| 1.0 | 25.4 | 58.6 | 75.0 | 58.96 | 62.80 |
| 1.5 | 25.4 | 56.0 | 63.63 | 57.00 | 53.10 |
| 2.0 | 25.4 | 54.4 | 57.80 | 55.20 | 41.40 |

Glow is a heterogeneous oxidative surface reaction that depends on the nature of burnt material and the oxygen available [14]

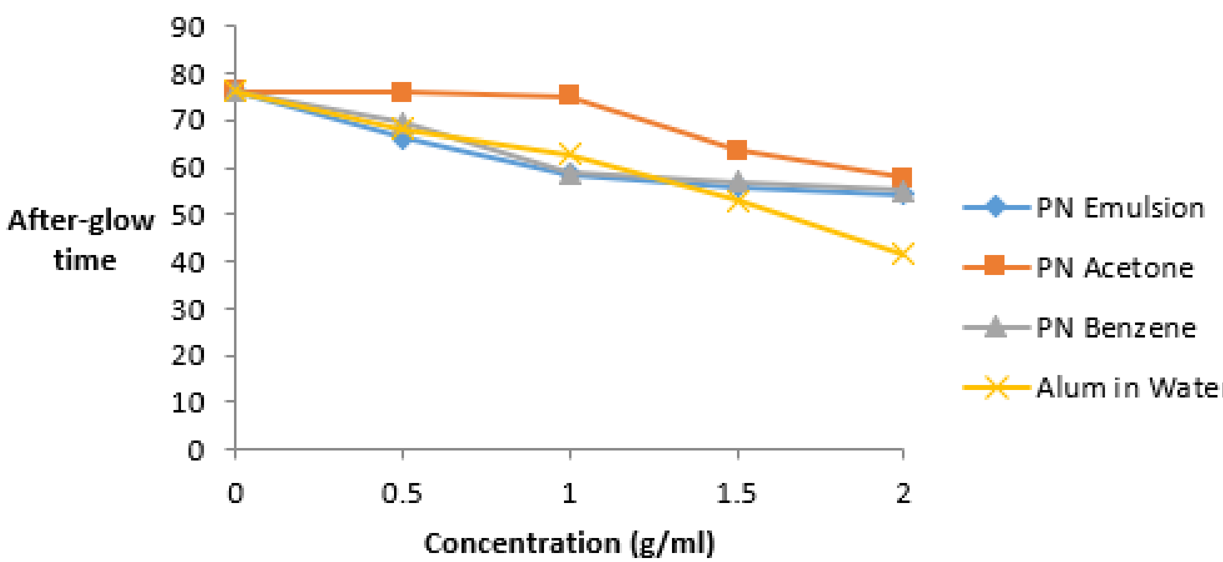


Figure 3. Effect of concentration of phthalonitrile and alum on after-glow time.

in water were measured against each concentration of phthalonitrile and alum. The result of the % char formation for phthalonitrile in all solvents and alum in water revealed that % char increases as the concentration increases [20]. The result in Table 4 below showed that the higher the amount of phthalonitrile and alum absorbed by the cotton fabric, the higher the % char and the greater the flame retardancy. According to Martel, the higher the number of residual chars after combustion, the lower the combustible or flammable volatiles to perpetuate the flame and the greater the degree of flame retardancy. Therefore, a high degree of flame retardancy is achieved by increasing the concentration of both phthalonitrile and alum on cotton fabric [21-22].

Table 4. Effect of phthalonitrile and alum concentration after flame time.

| C | PN in Emulsion | | | PN in Acetone | | | PN in Benzene | | | Alum in Water | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | WF | WC | PC | WF | WC | PC | WF | WC | PC | WF | WC | PC |
| 0 | 2.28 | 0.04 | 1.8 | 2.08 | 0.04 | 1.9 | 2.12 | 0.04 | 1.88 | 2.32 | 0.04 | 1.72 |
| 0.5 | 2.55 | 0.29 | 11.3 | 2.129 | 0.049 | 2.3 | 2.169 | 0.049 | 2.25 | 2.5 | 0.180 | 7.2 |
| 1.0 | 2.57 | 0.32 | 12.5 | 2.131 | 0.051 | 2.39 | 2.172 | 0.052 | 2.39 | 2.55 | 0.230 | 9.01 |
| 1.5 | 2.67 | 0.35 | 13.1 | 2.15 | 0.068 | 3.16 | 2.190 | 0.070 | 3.19 | 2.56 | 0.240 | 9.38 |
| 2.0 | 2.75 | 0.39 | 14.2 | 2.17 | 0.090 | 4.15 | 2.22 | 0.100 | 4.50 | 2.59 | 0.270 | 10.42 |

C – Concentration. (g/mL); WF - weight of fabric (g); WC - weight of char (g); PC – percent char (%)

Percent char formation of cotton fabric impregnated with PN in the emulsion in Figure 4 is higher than PN in acetone and PN in benzene due to the solvent effect. However, comparing the % char formation of the two flame retardants (phthalonitrile and alum), PN in emulsion had a better char forming ability (14.2%) because PN degrades thermally to produce incombustible gases which dilute combustible volatile gases of cotton fabric [7].

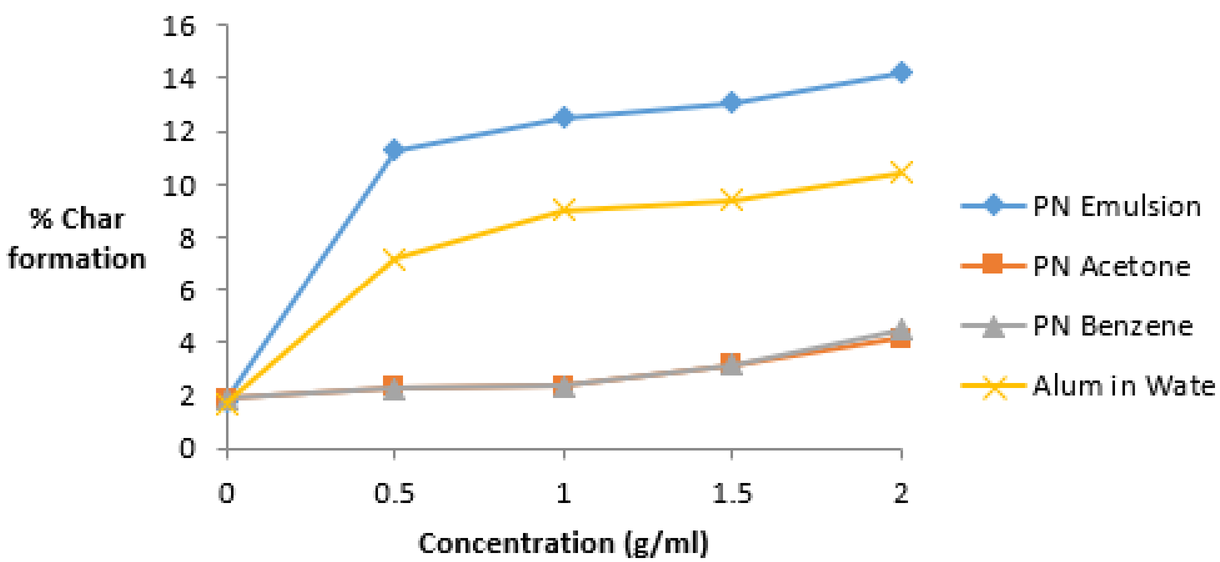


Figure 4. Effect of phthalonitrile and alum concentration on percent char formation.

## 4. Conclusion

Ordinarily, cotton fabrics are easily ignitable and highly flammable, which produce carbonaceous char, volatiles, and combustible gases on decomposition. Phthalonitrile, Benzene-1,2-carbonitrile, was employed to impart flame retardancy to 100% cotton fabric. Impregnating the fabric with phthalonitrile and alum solutions in different concentrations increased the ignition time after flame and char formation, while after-glow time decreased. It is assumed that the action of phthalonitrile under heat involves losing its constituent compounds and elements such as hydrogen cyanide, benzyl cyanide, nitrogen dioxide, nitrogen, and ammonia which are non-flammable gases within the flaming zone of the burning Polymer, playing the role of inert or not-easily oxidizable media, thus permitting flame retardancy.

The proportion of variations for phthalonitrile showed that it is a good flame retardant than alum. Phthalonitrile emulsion has a significant percent char formation than alum, while phthalonitrile in acetone and benzene has poor char formation.

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