

# THE ROLE OF NEWLY FORMULATED FIRE-RETARDANT SOLUTION ON THE PROTECTION OF LIFE

Hesham Reda\*

This study evaluated the effects of a number of newly formulated (guanylurea zinc phosphate GUZP) and commercial (phosphoric acid PA), fire retardant chemicals on the chemical and mechanical properties as well as fire resistance of jute fabric were tested. The chemical processing method used to formulate this fire retardant (called FR) results in an organic phosphate fire-retardant system with less acidic pH and fewer impurities. Results revealed that resistance of cellulosic fiber to fire increases in case of treatment with GUZP. No significant differences in thermal degradation between the untreated controls and the FR-treated cellulose were found in case of treatment with GUZP. Because of its milder acidity which results from the modified manufacturing process, enhanced stability related to thermal degradation was noted for this enhanced GUZP compared with PA. On exposure to elevated temperature, the strength and stiffness of FR-treated cellulosic fibers experienced slight deterioration. Treatments with antimony and zirconium salt results of samples of good fastness to washing and with significantly flame retardant.

## Introduction

The term "fire-resistance" designates to a compound or combination of compounds which decrease the flammability of a substrate to which it is added.<sup>(1)</sup>

Conventional materials (natural and man-made fibres, plastics, wood, paper etc.) used in everyday life are, in different degrees, liable to ignition. This fact has impelled the development of new materials which are inherently resistant to flame and heat or to modify these

- \* Associate Professor, Criminalistics Department, The National Center for Social and Criminological Research, Cairo, Egypt.

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materials by using flame-retardant additives/treatments to meet the stringent regulations set for fire protection.

Efforts on chemical modification of cellulose have been devoted principally to the study of compounds, reactions and processes which can decrease fabric flammability. Interest in this problem is not new, but recent legislation in the United States reflects heightened concern with fire safety, and growing needs for a broad spectrum of flame resistant textile products.<sup>(2)</sup> There are three main groups of flame retardant chemicals; a) inorganic eg. Metal hydroxides, antimony compounds, boron compounds and phosphorus compounds; B) halogenated products based primarily on chlorine and bromine; c) organophosphorus products which rely upon phosphate esters.

Only few studies have focused on in-service thermal degrade as affected by fire-retardants and post-treatment drying methods and that studies did not look at organic phosphate fire retardants.<sup>(3)</sup> Research has defined how much, when, and why fire retardants affect the properties of treated cellulose.<sup>(4)</sup> Models have been developed for predicting loss in bending strength of lumber and sheathing material.

Recently, an organic phosphate, phosphorus-nitrogen-boron multiplex fire retardant called FRW, which stands for fire retardant cellulose, was synthesized.<sup>(5)</sup> It is mainly composed of guanidyl urea phosphate (GUP), boric acid (B), and a minor amount of additives.

The flame retardant finishing of cellulosic fibers is of significance in diversified textile uses. According to the use in field and the use in textile, quite different requirements need to be made of a good wash fastness of the finishing. Considering the wash resistant finishing of cellulosic fibers, finishes on the base of phosphorus-nitrogen compounds prior important to the investigators,<sup>(6)</sup> amongst different types of non-resinous flame retardant finishes for cellulosic fibers, phosphorylation is reported to be of considerable importance as it imparts excellent flame resistant properties without influence on the handle of fabric. However, another possibility which

can impair the flame retardance property of phosphorylated cellulose is the non stability of phosphoric acid ester-bonds during soap-soda washing of the fabric. Metal oxides are known to reinforce the retardant property of cellulose in combination with phosphorus by forming complex with OH group of cellulose-phosphate and can be reduce ion-exchange considerably. From the total observation it may inferred that the ion exchange property of the phosphorylated cellulosic fibers impairs flame retardancy mechanism by formation of Ca and Mg phosphates during washing with hard water or soap-soda and a reduction of this ion-exchange effect can be achieved markedly by an after treatment of the phosphorylated cellulosic fibers with some metallic salts.<sup>(7)</sup>

The objective of this study was to look at the effect of a number of newly formulated (guanylurea zinc phosphate GZUP) and commercial (phosphoric acid PA), fire retardant chemicals on the chemical and mechanical properties as well as fire resistance of flax textile fabric. Also the effect of washing on phosphorus content after treatment of fibers with antimony and zirconium salt was also investigated.

## MATERIALS AND METHODS

### Preparation of Guanylurea Zinc Phosphate

The synthesis and structure of  $C_2H_7N_4O.ZnPO_4$  (guanylurea zinc phosphate) are reported. The cationic  $[C_2H_7N_4O]^+$  template was prepared in situ by the slow hydrolysis of the neutral 2-cyanoguanidine starting material. The resulting structure contains an unusual, unprotonated, zincophosphate layer topology as well as N-H...O template-to-template hydrogen bonds which help to stabilize a double sandwich of templating cations between the inorganic sheets.<sup>(8)</sup>

Textile made from flax fibers, size 10×10 cm was used. From the 350 samples, 125 pieces were randomly selected and used as

untreated controls, 75 others were treated with 10 percent phosphoric acid (PA), and the remaining 150 samples were treated with GUZP. A full-cell pressure process with final vacuum was used to impregnate the equilibrated specimens with the appropriate fire-retardant chemicals. In both the PA and GUZP treatments, the concentration of the chemical solution was 10 percent by weight for time intervals 2, 4, 6, 8, and 10 hours. Acidity was defined as pH value of the fire-retardant treating solution both before and after treatment and was determined by a Sartorius AG (Goettingen, Germany) PB-20 pH meter. The pH values of the GUZP solution before and after treatment were 4.0, and for the PA solution, the corresponding pH values were both 1.0.

At the end of each exposure, specimens were dried at 100 oC. Chemical component contents, including lignin, glucan, and other sugars, were also measured during the exposure time using procedures developed by Davis, 1998.<sup>(9)</sup> Fire tests was conducted in accordance with ASTM Standard E 119.<sup>(10)</sup> Two point static bending tests were conducted on board specimens as per ASTM 790 M using 160 mm span and a head speed of 4.3 mm/minute to determine modulus of rupture (MOR) and modulus of elasticity (MOE).<sup>(11)</sup>

After treatments and measuring the above mention results, the samples with optimum conditions were padded with a solution containing a combination of antimony oxide and zirconium oxy-chloride with a liquor up to 50%. The fabrics were batched for 5 minutes and subsequently treated with 15 % sodium carbonate solution to neutralize the acidity. The samples were then washed thoroughly in running cold water at room temperature.

In a single washing treatment, the samples were boiled for 30 minutes in a solution containing 3 g/l soap and 1.5 g/l soda ash. Phosphorus content in the treated samples was determined according to method suggested by Basch.<sup>(12)</sup>

## RESULTS AND DISCUSSION

Table (1) illustrates the chemical and mechanical properties of untreated flax fabric textile.

### Flame resistance effects

In the ASTM E84 25-foot tunnel furnace test for measuring flame spread of building materials, an igniting pilot flame is applied to the underside of a horizontally mounted specimen.<sup>(13)</sup> The flame heats the combustible material to pyrolysis, and the flammable gases given off are ignited by the pilot flame. If the pyrolysis-combustion process becomes exothermic, the flaming on the specimen becomes self-propagating. A flame-spread classification or rating number is calculated from the time-distance progress of the flame along the length of the specimen surface.

Fig. (1) shows the flame resistance by treated textile as a result of fire treatment with newly formulated chemicals (guanylurea zinc phosphate GUZP) and commercial (phosphoric acid PA). Compared with PA, treated textile with GUZP showed remarkable resistance to fire up to 44 minutes at exposure time 8 hours, while it showed resistance to fire up to 23 minutes in case of treatment with PA at exposure time 4 hours. This may be attributed to the nature of phosphorus containing agent used for treatment. In the presence of some nitrogen compounds, the minimum phosphorus content required for self extinguishing behavior is significantly lower, indicating synergistic interaction of phosphorus and nitrogen in inhibiting formation of flammable decomposition products during thermal degradation of the cellulose.<sup>(14)</sup>

### Effects on chemical composition of flax fabrics

Compare with chemical compositions of untreated flax textile fabric, as given in Table (1) treated samples with PA at different time

intervals showed remarkable decrease in a-cellulose and hemicellulose as shown in Table (2) Conversely, lignin residues increased during the course of exposure time. We feel this apparent increase in lignin might simply be a remnant of the fact that the relative content of total weight of lignin rises as sizable losses occur in polysaccharide content from acid degradation. Comparing the relative rate of increase in lignin to the relative rate of loss in hemicelluloses seems to confirm our suspicion.

Chemical compositions of textile fabrics treated with GUZP were also reported in Table (2) Although there are some irregularities, no remarkable change were recognized in the chemical compositions in the textile fabrics with increasing the exposure time. These results are in agreements with the previous works that highly acidic PA-treated specimens showed the most changes in cellulose components.<sup>(15)</sup>

#### **MOE and MOR treatment effects**

Figs (2 and 3) show the effect of exposure time on MOE and MOR of flax textile fabrics treated with GUPZ and PA. Similarly to chemical compositions, treatments with GUPZ illustrate no significant decrease in either MOE or MOR compared with control values for all course of exposure. Accordingly to slower property degradation noted for GUPZ may in turn result in even longer service lives for flax treated materials exposed at different time intervals.

With respect to fabrics treated with PA, increasing the exposure time was contributed to the decrease in both MOE and MOR. This severe degradation in bending strength is related to stronger acidity of PA with great impurities compared with GUPZ.

#### **Effect of adding metal oxide**

During phosphorylation of flax fabrics to different levels of phosphorus content it was observed that the fabric showed excellent flame

retardant properties. But simultaneously, it was found that when the samples were washed in hard water or with soda-soap, the fabrics failed in flame retardancy. This had been mainly attributed to the ion exchange property of the phosphorylated flax.

This ion-exchanged cellulose phosphate is converted to alkali metal phosphate during heating and does not release phosphorus at pyrolytic temperature of cellulose, which in turn impairs the flame retardancy mechanism and thus cellulose fibers burn.

After treatment with metal oxide the samples gave entirely different results. Table (2) revealed that treatment of phosphorylated flax with solution containing antimony oxide and zirconium oxy-chloride result in flame retardancy up to 6 washes in case of samples treated with GUZP for 8 hours, and up to 4 washes in case of samples treated with PA for 4 hours. This may be attributed to ion-exchange phenomenon may be suppressed by the blocking of the P-OH groups in phosphorylated flax to some extent.<sup>(19)</sup>

#### **AKNOWLEDGMENT**

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**Table (1)**  
**Chemical and mechanical properties**  
**of untreated flax textile fabric**

|                         |      |
|-------------------------|------|
| Klason Lignin (%)       | 14   |
| $\alpha$ -cellulose (%) | 63   |
| Hemicellulose (%)       | 24   |
| MOE (MPa)               | 6.2  |
| MOR (GPa)               | 41.0 |

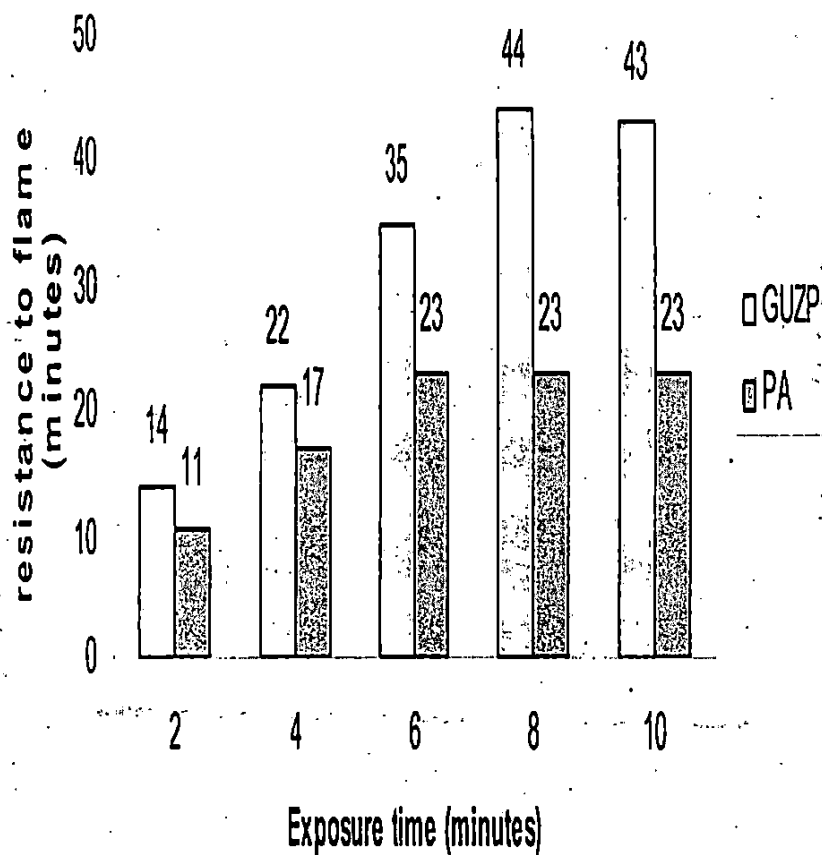
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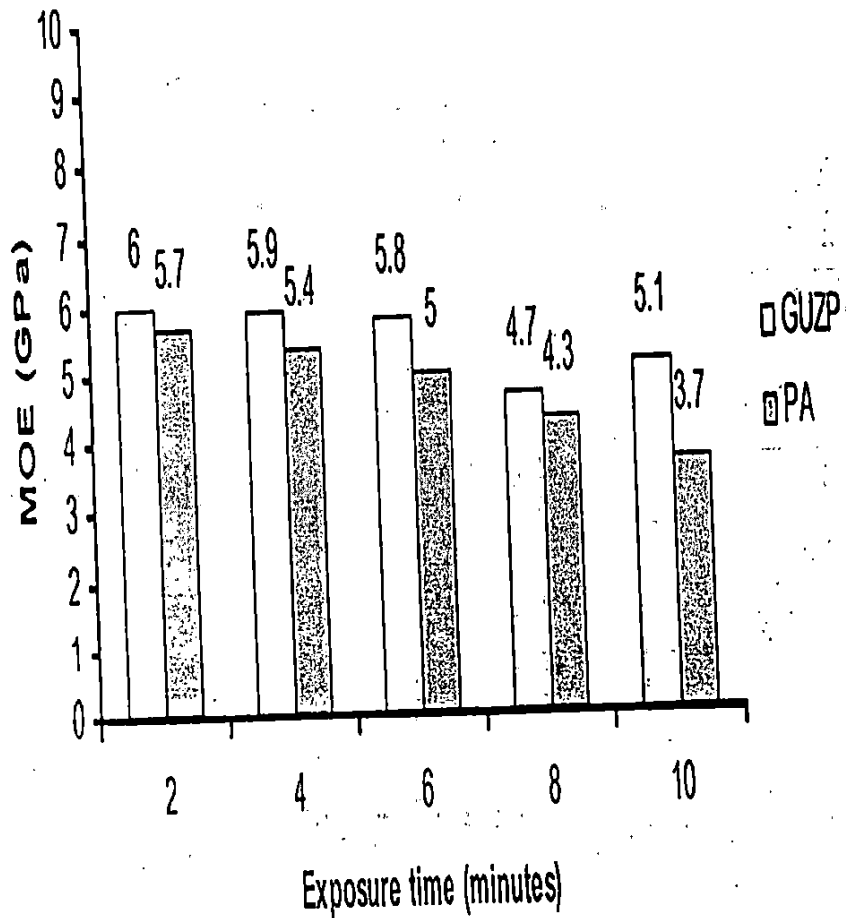
**Table (2)**  
**Percentage of total chemical composition of treated**  
**flax textile fabric with (PA and GUZP) at different exposure time**

| Exposure<br>hours | PA                      |                                |                           |                       | GUZP                    |                                |                           |                       |
|-------------------|-------------------------|--------------------------------|---------------------------|-----------------------|-------------------------|--------------------------------|---------------------------|-----------------------|
|                   | Klason<br>lignin<br>(%) | $\alpha$ -<br>cellulose<br>(%) | Hemi-<br>cellulose<br>(%) | Total<br>Yield<br>(%) | Klason<br>lignin<br>(%) | $\alpha$ -<br>cellulose<br>(%) | Hemi-<br>cellulose<br>(%) | Total<br>Yield<br>(%) |
| 2                 | 14.43                   | 58.45                          | 22.18                     | 95.06                 | 13.02                   | 60.20                          | 23.74                     | 96.96                 |
| 4                 | 15.48                   | 57.04                          | 20.20                     | 92.72                 | 13.20                   | 59.76                          | 22.12                     | 95.08                 |
| 6                 | 16.20                   | 52.78                          | 18.98                     | 87.96                 | 14.62                   | 59.66                          | 21.76                     | 96.04                 |
| 8                 | 16.76                   | 50.23                          | 17.96                     | 84.95                 | 15.30                   | 59.20                          | 21.45                     | 95.95                 |
| 10                | 17.43                   | 47.25                          | 16.78                     | 81.46                 | 15.82                   | 58.90                          | 20.28                     | 95.00                 |

(Fig. 1): Effect of exposure time on the resistance to flame



(Fig. 2): Effect of exposure time on the MOE of flax textile treated with GUZP and PA



(Fig.3): Effect of exposure time on the MOR of flax textile treated with GUZP and PA

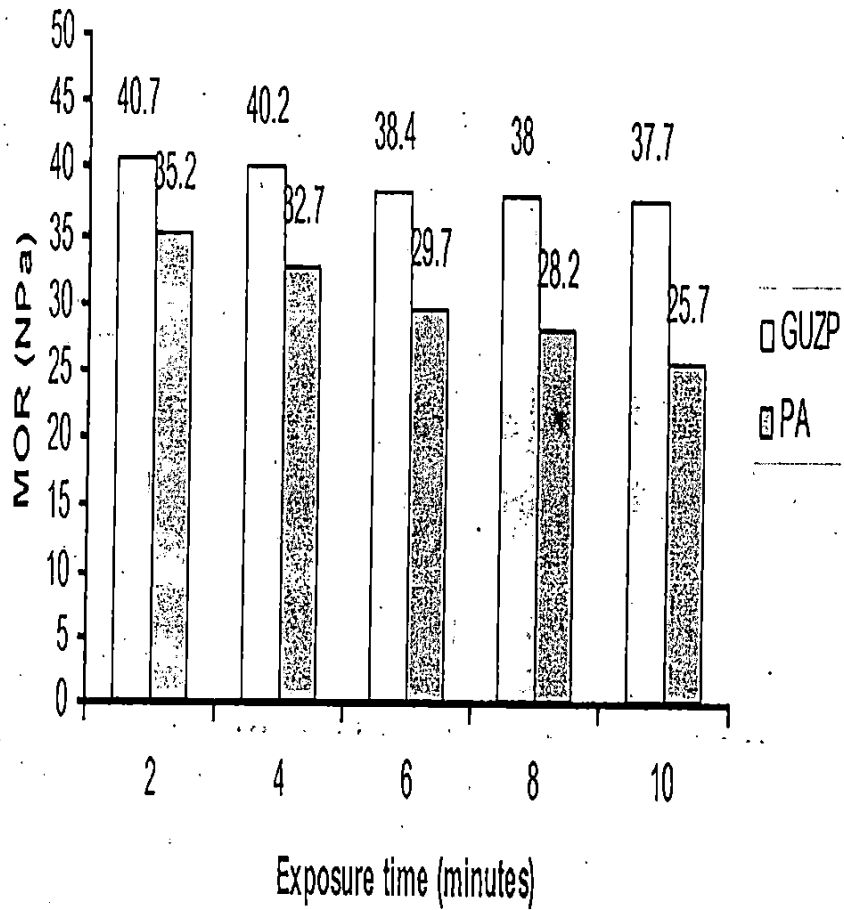
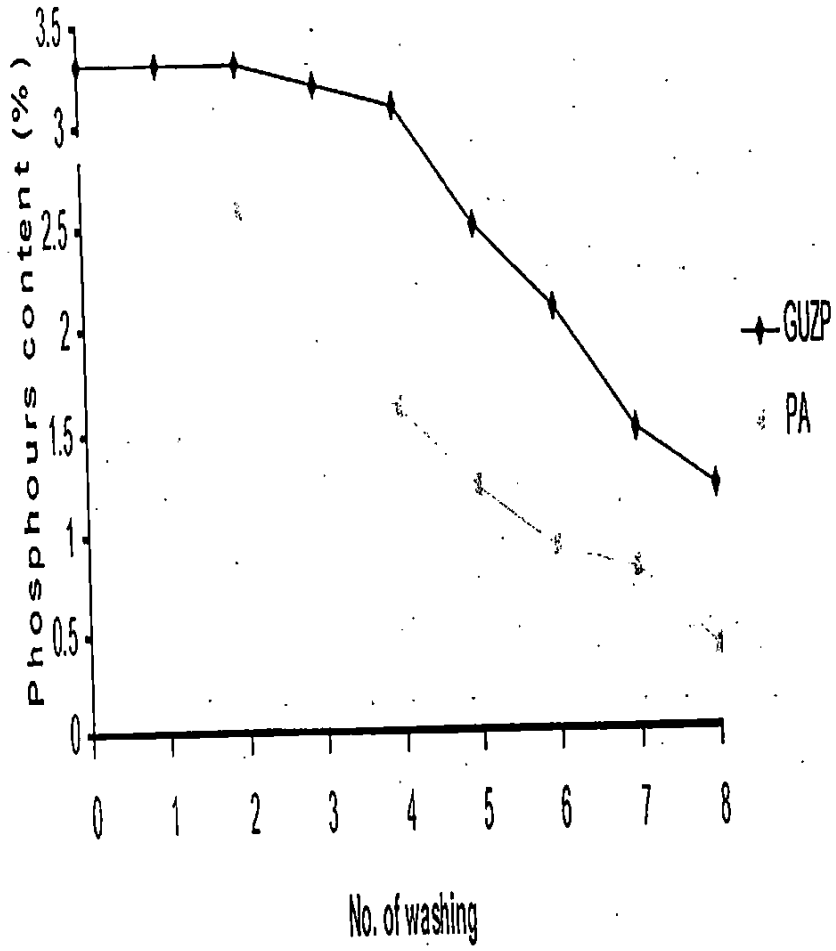


Fig. 4: effect of no. of washing on the phosphours content of flax textile treated with GUZP and PA at different exposure time



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## دور المحاليل المؤخرة للهبافى حماية الأرواح

### هشام رضا

من المعروف أن بعض المواد المصنعة - مثل الأخشاب والأقمشة وخلافه - قابلة للاشتعال عند تعرضها للهب . هذه الحقيقة تقودنا إلى استعمال محاليل ترش على هذه المواد لتأخير زمن اشتعالها إلى أطول فترة ممكنة .

تم فى هذا البحث تصنيع مادة كيميائية جديدة (جوانيل يوريا فوسفات الزنك GUZP) تستعمل كمؤخرات للهب ، وتم معالجة أقمشة مصنعة من ألياف الكتان بهذه المحاليل عند فترات زمنية مختلفة ، وقياس مدة تحملها للهب ، والتغير بالخواص الميكانيكية والكيميائية لهذه الأقمشة ، ومقارنتها بنتائج تعريض هذا النوع من الأقمشة لمحاليل تجارية مؤخرة للهب (حمض الفوسفوريك PA) . حيث أثبتت النتائج أن ألياف الكتان المعالجة بـ GUZP تتحمل الهب لفترات أطول حيث تزيد من الثبات الكيميائى للألياف ، وتؤدى إلى عدم تأثر الخواص الميكانيكية لها مقارنة بالألياف المعالجة بالمحاليل التجارية .

كما أثبتت النتائج أن الألياف المعالجة بـ GUZP عند تعريضها لمخلوط من أكسيد الأنتيمون وكلوريد الزركونيوم يمكن أن تتحمل التغير بالظروف الجوية لفترات أكثر من الألياف المعالجة بالمحاليل التجارية .