

[54] **FLAME PROOFING OF FABRICS**  
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[56] **References Cited**

| UNITED STATES PATENTS |         |                     |         |
|-----------------------|---------|---------------------|---------|
| 1,837,150             | 12/1931 | Dreyfus et al. .... | 117/138 |
| 2,530,261             | 11/1950 | Morton et al. ....  | 117/137 |
| 3,092,537             | 6/1963  | Brandts. ....       | 162/159 |
| 3,409,386             | 11/1968 | Bloch et al. ....   | 117/137 |

3,436,250 4/1969 Kyoto et al. .... 117/137  
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[57] **ABSTRACT**  
Normally flammable textile fabrics composed of polyamides such as polyhexamethylene adipamides, polycaproamides, poly(m-phenylene isophthalamides) and the like, are rendered highly flame proof by the intimate association therewith of a flame proofing amount of an ammonium acid phosphate, especially monoammonium diacid phosphate. Amounts of ammonium acid phosphates of at least, and preferably in excess of 0.4 percent by weight (in terms of phosphoric acid equivalent) increase the Oxygen Index of the treated fabrics to over 40, and the treated fabrics are non corrosive and non-irritating in nature.  
**21 Claims, No Drawings**

## FLAME PROOFING OF FABRICS

### FIELD OF INVENTION

This invention relates to improvements in the flame proofing of normally flammable fabrics. More particularly it relates to the treatment of normally flammable fabrics composed of certain synthetic polymers and especially it relates to fabrics composed of poly(m-phenyleneisophthalamides) which have been treated to increase the Oxygen Index of said fabrics to at least 40.

### BACKGROUND OF THE INVENTION

Apparel for use in applications where under emergency conditions a hazardous thermal environment might exist should satisfy the following minimum requirements.

- The fabric from which the apparel is made should be resistant to burning, melting or disintegration on exposure to open flames or elevated temperatures.
- The fabric should possess good dimensional stability on exposure to elevated thermal conditions since large thermal shrinkages tend to restrict mobility of the wearer.
- The apparel should function as an effective thermal barrier in order to prevent severe skin burns, and
- The garments should be durable, non-irritating, and comfortable to encourage their use.

It is known to treat normally flammable textile materials, of both natural and synthetic nature, with chemicals such as triammonium phosphate, tetrakis(hydroxymethyl) phosphonium oxides and polymers thereof, and the like to render them fire retardant. Such treatments while effective for rendering fabrics fire retardant under normal conditions of use, such as fabric designed for use as curtains, rugs, sweaters and the like, are not satisfactory for use under emergency or highly hazardous conditions as in aviators flying suits or apparel designed for use in oxygen enriched atmospheres.

Synthetic materials, such as polybenzimidazoles and polyamides such as poly(m-phenyleneisophthalamides) which exhibit improved heat resistance compared to other synthetics such as polypropylene and polyamides such as polyhexamethylenedipamides and polycapromamides are known and these improved fibers have replaced the more conventional fire retardant materials in many special applications. In copending application Ser. No. 230,999, filed Mar. 1, 1972, now abandoned it is disclosed that normally flammable fabrics such as polypropylene and polyamides could be rendered flame proof by the intimate association therewith of a flame proofing amount of a phosphoric acid. Such treated fabrics, although substantially improved with respect to their resistance to the propagation of flames, are somewhat corrosive to metals and tend to cause irritation to the skin of those wearing clothing fabricated from such treated fabrics. Accordingly a need still exists for a fiber with thermal characteristics superior to those of the aforementioned fibers and which are non corrosive and non irritating in character.

### OBJECTS OF THE INVENTION

It is, therefore, a principal object of this invention to devise improved flame proofed textile fabrics comprising normally flammable synthetic materials.

Another object is to provide a process for treating normally flammable synthetic materials to render them

non-corrosive and non-irritating as well as flame proof.

A particular object is to devise compositions of normally flammable synthetic materials comprising an effective flame proofing amount of an ammonium acid phosphate intimately associated therewith.

These and other objects of the present invention will be obvious from the following description.

### BRIEF SUMMARY OF THE INVENTION

In accordance with the present invention, normally flammable fabrics of synthetic polymers are rendered highly flame proof by intimately admixing the fabric with an effective flame proofing amount of an ammonium acid phosphate. The resultant treated fabric is not only surprisingly fire proof but also non-corrosive and non-irritating in character.

By "effective flame proofing amount" is meant that amount of an ammonium acid phosphate which suffices to increase the Oxygen Index of the treated material to 40 or above.

By the term "Oxygen Index" it is intended to define the percentage concentration of oxygen in a mixture of oxygen and nitrogen which will maintain equilibrium burning conditions, i.e., the heat produced during combustion just balances the heat lost to the surroundings. Physically, the Oxygen Index is the lowest concentration of oxygen, in an atmosphere of oxygen and nitrogen, which will support sustained combustion of the material and is calculated from the following equation

$$\text{Oxygen Index} = \frac{100 \times \text{O}_2}{\text{O}_2 + \text{N}_2}$$

where  $\text{O}_2$  is the oxygen concentration at equilibrium and  $\text{N}_2$  is the associated nitrogen concentration. (See "The Oxygen Flame Flammability Test," J. L. Isaacs, J. Fire and Flammability, Vol. 1 (January 1970) page 36 et seq.)

In the practice of the present invention, the materials treated may be formed in whole or in part of normally flammable synthetic polymer material and may be in various forms including yard or sheet goods, as well as various finished articles, such as articles of clothing including coats, shirts, trousers, skirts, jump suits, gloves, and the like. The materials may be woven, non woven, knitted, and the like. Accordingly although, hereinafter primary reference will be made to the treatment of fibrous woven synthetic polymer yard goods, this is not to be taken as a limitation as other forms of synthetic polymer materials, such as non-woven, films, foils, sheets, fibers and yarns, may, in many instances, be utilized as the materials treated in accordance with the present invention.

### DETAILED DESCRIPTION OF THE INVENTION

In accordance with a preferred mode of carrying out the present invention normally flammable synthetic polymers, such as polycapromamides, polyhexamethylene adipamides and poly(m-phenylene isophthalamides) having intimately associated therewith an effective flame proofing amount of a phosphoric acid, and thus have been rendered flame proof in character, are reacted, in situ with gaseous ammonia until the treated fabric is substantially neutral in reaction, i.e. a pH of about 7.

It has been found as disclosed in the aforementioned Ser. No. 230,999, that normally flammable synthetic polymers which contain, intimately mixed therewith, at least about 0.4 percent by weight, and preferably from about 2 to about 25 percent by weight, of a phosphoric acid, preferably ortho phosphoric acid or pyrophosphoric acid, and rendered flame proof, that is the Oxygen Index of the treated synthetic polymer has been increased to about 40 or higher.

The flame proofing treatment of this invention can be accomplished by several means. For example the synthetic material, in the fibrous or woven condition, can be immersed, padded, sprayed, or dipped in or with an aqueous solution of a phosphoric acid, the thoroughly wetted material dried to remove excess moisture and, then exposed to gaseous ammonia vapors until the material reacts neutral. The treated fabric may be heated to below the decomposition point of the synthetic polymer without significant effect on the treatment.

Alternatively, the material can be treated with an aqueous solution of monoammonium diacid phosphate or less preferably diammonium monoacid phosphate to thoroughly impregnate the material. Thereafter the treated material containing an amount of the ammonium acid phosphate salt which is at least about 0.4 percent by weight, dry basis and in terms of phosphoric acid equivalent can be dried in a conventional manner.

Alternatively the phosphoric acid treatment can be effected by application of a solvent solution of elemental white phosphorus and thereafter the solvent evaporated under relatively mild conditions. Also, the polymer material may be exposed to vapors of phosphorus and thereby phosphorus is condensed on the surface of the material. The elemental phosphorus residue can then be oxidized on the fibrous material and hydrolyzed to pyrophosphoric acid in a known manner. "White phosphorus" as used herein includes various impure and commercial grades sometimes referred to as "yellow phosphorus".

The solvents used to assist in the application of the elemental white phosphorus to the polymer material should be one or a mixture of organic solvents which do not react with the material or the phosphorus, and should be readily removable from the treated material. Typical of such solvents are carbon disulfide, chloroform, trichloroethylene, benzene and the like. Trichloroethylene because of its non-reactive nature and ease of removal is the preferred solvent for the elemental white phosphorus.

The treatment can be carried out using cold or hot solutions of the phosphoric acid and with either dilute or concentrated solutions of the treatment acid. Conveniently 85 percent ortho phosphoric acid is used although higher or lower concentrations are useful also.

Any of the inorganic phosphoric acids can be used. Thus ortho, meta-, or pyrophosphoric acids and mixtures thereof are contemplated for use in the process of the present invention. Ortho phosphoric acid because of its general availability and effectiveness is preferred. As indicated above, the phosphoric acid can be applied to the synthetic polymer by first impregnating the material with elemental phosphorus and thereafter oxidizing the elemental phosphorus on the fiber and hydrolyzing the oxidized phosphorus. This procedure probably results in the formation of a mixture of phosphoric acids, but for convenience, it is presumed that hydro-

lyzed product is essentially pyrophosphoric acid and such will be so-called hereinafter.

As will be apparent from the above discussion, the application, introduction, impregnation or other means of obtaining the phosphorus compound-polyamide material composition can be effected in several ways. Thus the phosphoric acid can be admixed with the polyamide material directly and thereafter the acid can be converted to the ammonium acid phosphate salt, or mixtures thereof, in situ by exposure to gaseous ammonia or elemental phosphorus can be applied to the polyamide material oxidized thereon to a phosphoric acid compound and converted to the ammonium acid phosphate with gaseous ammonia, or the ammonium acid phosphate salt can be applied directly to the polyamide material. In each instance an effective fire retardant amount of phosphoric acid or an amount of ammonium acid phosphate salt containing the equivalent of such a fire retardant amount of phosphoric acid is applied to the polyamide material. It is preferred to apply the phosphoric acid to the polyamide material and convert the acid to the ammonium acid salt(s) in situ, since it has been found that by this procedure the highest Oxygen Indexes are obtainable.

Although the flame proofing treatment of this invention initially results in fabrics having an Oxygen Index of at least 40, this value has been found to decrease as a result of repeated washing of the treated fabric. It has been found, as disclosed in the above noted copending application, that the treatment in accordance with this invention can be stabilized, that is flame proofing treatment can be rendered more fast to washing, by applying to the treated material a coating of synthetic resin material, having an Oxygen Index of at least 40. Such a resin is for example polyvinylidene chloride. Perfluorinated organic polymers, such as Teflon, can be used also.

It has thus been found that by dipping, immersing, spraying, roller coating or otherwise applying to the surface of a treated synthetic polymer material of this invention a solvent solution of polyvinylidene chloride or the like polymer, and evaporating the solvent, a coating of the resin is applied to the surface of the treated polymer material and the flame proofing character of the treated material is thereby rendered more fast to washing.

Solvents suitable for use in this manner, include by way of examples such solvents as dioxane, cyclohexanone, tetrahydrofuran, dimethylformamide and ethylacetate.

The following examples will illustrate the present invention. Parts and percentages are by weight and temperatures are given in degrees centigrade unless otherwise specified.

#### EXAMPLE I

A. A strip measuring about one-fourth inch by two inches of a woven poly(m-phenyleneisophthalamide) fabric (dark blue dyed "shirt fabric") was immersed in an aqueous 85 percent ortho-phosphoric acid bath. The wetted strip was dried in a current of heated air to the point of bubbling of the adherent phosphoric acid on the surface of the fabric. The partially dried material was rinsed in running water and then dried in a current of heated air.

The Oxygen Index of the treated fabric determined as described in J. Fire and Flammability, Vol. 1 (January 1970) page 36, was  $59 \pm 1$ .

An untreated fabric strip of the same synthetic material had an Oxygen Index of  $29 \frac{1}{2} \pm \frac{1}{2}$ .

The treated fabric strip was exposed to ammonia vapor for a brief period, sufficient to render the surface of the fabric neutral to pH indicator paper (grass green color of Hydrion A Indicator paper). The Oxygen Index of the neutralized fabric was  $59 \pm 1$ .

B. The procedure described above was repeated using a 20 percent aqueous orthophosphoric acid bath to impregnate the synthetic material. The Oxygen Index of this material after rinsing and drying was  $63 \pm 1$ .

This treated fabric strip was exposed to ammonia fumes in a closed container to neutralize the phosphoric acid. The Oxygen Index of the neutralized fabric strip was found to be unchanged, i.e., O.I = 63.

### EXAMPLE II

Several strips, measuring  $1/4$  inch by two inches of woven poly(phenyleneisophthalamide) fabric (dark blue dyed shirt fabric) were treated as follows:

One strip was immersed in a 10 percent aqueous monoammonium diacid phosphate solution.

One strip was immersed in a 20 percent aqueous monoammonium diacid phosphate solution.

One strip was immersed in a 10 percent aqueous diammonium acid phosphate solution.

One strip was immersed in a 20 percent aqueous diammonium acid phosphate solution.

Each of the strips was then dried in a current of heated air.

The Oxygen Index of each of the so treated fabric strips was determined, and the values obtained are set out in the following table.

TABLE

| Agent                              | Oxygen Index |              |
|------------------------------------|--------------|--------------|
|                                    | 10% Solution | 20% Solution |
| $\text{NH}_4\text{H}_2\text{PO}_4$ | 56           | 59           |
| $(\text{NH}_4)_2\text{HPO}_4$      | 53           | 56           |

It can thus be seen that impregnation of poly(m-phenylene isophthalamides) with ammonium salts of phosphoric acid is an effective means of increasing the Oxygen Index of normally flammable textile fabrics composed of polyamides.

The invention has been described in the above specification and illustrated by reference to specific embodiments in the illustrative examples. However it is to be understood that it is not to be so limited since changes and alterations in the specific details disclosed hereinabove may be made without departing from the scope or spirit of the invention disclosed herein.

What is claimed is:

1. Flame proofed synthetic fabric consisting essentially of a normally flammable synthetic material selected from the group consisting of poly(hexamethylene adipamide), polycaproamide, and poly(m-phenyleneisophthalamide) which material contains a flame retardant amount of a ammonium salt of phosphoric acid, selected from the group consisting of mono and diammonium acid phosphate and mixtures thereof.

2. Flame proofed synthetic fabric as claimed in claim 1 wherein the material comprises at least 0.4 percent by weight of a phosphoric acid, which has been neutralized by ammonia gas.

3. Flame proofed synthetic fabric as claimed in claim 2 wherein the material comprises from about 2.0 to about 25 percent by weight of a phosphoric acid, which has been neutralized by ammonia gas.

4. Flame proofed synthetic fabric as claimed in claim 2 wherein the phosphoric acid is ortho phosphoric acid.

5. Flame proofed synthetic fabric as claimed in claim 2 wherein the phosphoric acid is pyrophosphoric acid.

6. Flame proofed synthetic fabric as claimed in claim 2 wherein the synthetic material is poly(m-phenyleneisophthalamide).

7. Flame proofed synthetic fabric as claimed in claim 1 wherein the synthetic material is poly(m-phenyleneisophthalamide).

8. Flame proofed synthetic fibrous fabric as claimed in claim 3 wherein the synthetic material is poly(m-phenyleneisophthalamide) and the phosphoric acid is ortho-phosphoric acid.

9. The process which consists essentially of the steps of treating a fabric consisting essentially of a normally flammable synthetic polymer material selected from the group consisting of poly(hexamethylene adipamide), polycaproamide, and poly(m-phenyleneisophthalamide) with a phosphoric acid to deposit a flame retarding amount of said phosphoric acid on the polymer material, and neutralizing the phosphoric acid with ammonia gas.

10. The process as described in claim 9 wherein the polymer is poly(m-phenyleneisophthalamide).

11. The process as described in claim 10 wherein the treated fabric has an Oxygen Index of at least about 40.

12. The process as described in claim 11 wherein the treated fabric has an Oxygen Index of from 50 to about 60.

13. The process of applying a fire retardant amount of an acid ammonium salt of a phosphoric acid to a normally flammable synthetic polymer material which consists essentially of:

a. applying elemental white phosphorus to a fabric consisting essentially of a normally flammable synthetic polymer material selected from the group consisting of polyhexamethylene adipamide, polycaproamide, and poly(m-phenyleneisophthalamide),

b. Oxidizing the phosphorus on the material,

c. hydrolyzing the oxidized phosphorus on the material to pyrophosphoric acid, the amount of phosphorus applied in step (a) being sufficient to provide a fire retardant amount of pyrophosphoric acid after hydrolysis, and

d. neutralizing the pyrophosphoric acid with gaseous ammonia.

14. The process as claimed in claim 13 wherein the normally flammable synthetic polymer material is poly(m-phenyleneisophthalamide).

15. The process as claimed in claim 14 wherein the elemental white phosphorus is applied to the polymer material as an organic solvent solution and the organic solvent is removed by evaporation prior to oxidizing the phosphorus.

16. The process as claimed in claim 15 wherein the organic solvent is trichloroethylene.

17. The process of impregnating a fabric consisting essentially of a normally flammable synthetic polymer material selected from the group consisting of polyhexamethylene adipamide, polycaproamide and poly(m-phenyleneisophthalamide) with a fire retardant amount of an ammonium salt of phosphoric acid selected from the group consisting of monoammonium acid phosphate acid and diammonium acid phosphate acid which consists essentially of immersing the polymer material in an aqueous solution of said ammonium salt and drying the polymer material.

18. The process of claim 17 wherein the polymer material is poly(m-phenyleneisophthalamide).

19. The process of claim 17 wherein the ammonium

salt is monoammonium acid phosphate.

20. The process of claim 17 wherein the ammonium salt is diammonium acid phosphate.

21. A process for increasing the Oxygen Index of a fabric consisting essentially of a normally flammable synthetic polymer material selected from the group consisting of poly(hexamethylenedipamide), polycaproamide, and poly(m-phenyleneisophthalamine) which consists essentially of applying to said polymer material a flame retarding amount of at least one ammonium salt of phosphoric acid selected from the group consisting of mono and diammonium acid phosphate.

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