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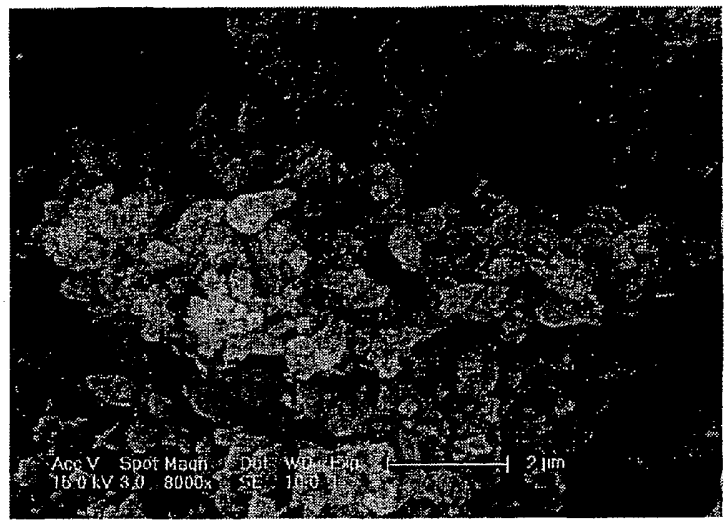
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(54) Title: GAS PHASE SYNTHESIS OF POLYHYDRIDE PHOSPHORUS POLYMERS



(57) Abstract: A polyhydride phosphorus polymer is produced by subjecting phosphine to gas phase synthesis. The gas phase synthesis is carried out using a free radical as a gas phase initiator. The polyhydride phosphorus polymer can be deposited on an article of manufacture by adjusting amounts of NO and phosphine in a sealed vessel so as to deposit the polyhydride phosphorus polymer at a desired rate. The deposited polyhydride phosphorus polymer can be subjected to oxidizing by an oxidizing medium such as a. solution of hydrogen peroxide. A heat/fire resistant coating produced by. the oxidizing can be used on articles such as flammable textile materials such as drapery, clothing and carpeting or articles of manufacture such as oven/ furnace parts, building materials, electronic components, automobile and aircraft parts.

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GAS PHASE SYNTHESIS OF POLYHYDRIDE PHOSPHORUS POLYMERS

FIELD OF THE INVENTION

The invention relates to gas phase synthesis of a polyhydride phosphorus polymer, conversion thereof to a heat/fire resistant film/coating and articles incorporating same.

SUMMARY

A method of making a polyhydride phosphorus polymer comprises subjecting phosphine gas to gas phase synthesis. The gas phase synthesis preferably utilizes a free radical such as nitric oxide or nitrous oxide as an initiator. Phosphine gas may be generated at point of use by exposure of a metal phosphide such as, for example, magnesium phosphide, calcium phosphide or aluminum phosphide, to ambient humidity. For example, the polyhydride phosphorous polymer can be formed in a sealed vessel by adjusting amounts of PH_3 and NO to deposit the polyhydride phosphorus polymer at a desired rate.

The polyhydride phosphorus polymer can be used as an intermediate product to make other phosphorus compounds. For example, the polyhydride phosphorus polymer can be deposited on a substrate such as an article of clothing or on a part intended for use in a high temperature environment. The polyhydride phosphorus polymer can be converted to a heat/fire resistant film/coating by oxidizing the polyhydride phosphorus polymer. For example, the polyhydride phosphorus polymer can be oxidized in a gaseous environment or by contacting the polyhydride phosphorus polymer with a solution of hydrogen peroxide. In the case of an article coated with the polyhydride phosphorus polymer, the coated article can be immersed in a solution of hydrogen peroxide to oxidize the polyhydride phosphorus polymer preferably to a polymeric phosphine oxide film/coating.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a scanning electron microscopy image of a polyhydride phosphorus polymer formed in via gas phase synthesis; and

Figure 2 shows elemental analysis of the polyhydride phosphorus polymer shown in Figure 1.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Yellow amorphous polyhydride phosphorus polymers (P_xH_y wherein x and y are each greater than 1) can be formed via gas phase synthesis. These solid phosphorus hydrides are highly polymeric and are insoluble in common solvents.

In a preferred embodiment, the gas phase synthesis of polyhydride phosphorus polymers involves phosphine gas interaction with an initiator such as nitric oxide (NO) and/or nitrogen dioxide (NO_2) (from the oxidation of NO) promoting the polymerization. However, the polyhydride phosphorus polymer can be produced by any suitable gas phase synthesis technique. The gas phase synthesis can be carried out by introduction of a controlled amount of NO gas into a sealed vessel containing a controlled amount of phosphine gas so as to promote formation of this yellow, amorphous and highly polymeric phosphorus polymer, P_xH_y. While not wishing to be bound by theory, a proposed mechanism of this free radical induced polymerization from the relatively stable NO radical is as follows:

PH_3	+	$\cdot NO$	→	$\cdot PH_2$	+	HNO
phosphine		nitric oxide		phosphine radical		nitrosyl hydride

PH_3	+	$\cdot PH_2$	→	P_2H_4	+	H
phosphine		phosphine radical		diphosphine		hydrogen atom

While not wishing to be bound by theory, it is believed that nitric oxide abstracts a proton from phosphine resulting in the phosphine radical and nitrosyl hydride. According to this theory, nitrosyl hydride ultimately becomes nitric acid and the phosphine radical polymerizes with phosphine gas upon gas phase collision with a phosphine molecule. The polymerization then continues with the collision of subsequent phosphine radicals generated from nitric oxide and or nitrogen dioxide. A "living" phosphine polymer is also a possibility. This reaction can be demonstrated by the introduction of nitric oxide gas (~2% in nitrogen) into an 0.2 m^3 (8 ft^3) sealed vessel containing ~1000 ppm of phosphine gas in air under ambient temperature and pressure conditions.

Figure 1 shows a scanning electron microscopy photomicrograph of the polyhydride phosphorus polymer produced in the vessel. The elemental analysis of the polyhydride phosphorus polymer is shown in Figure 1 wherein background spectra is not included.

In a method of making a polyhydride phosphorus polymer, phosphine gas can be subjected to gas phase synthesis with a free radical such as nitric oxide or nitrous oxide. Phosphine gas may be generated at point of use by exposure of a metal phosphide such as, for example, magnesium phosphide, calcium phosphide or aluminum phosphide, to ambient humidity. For example, the polyhydride phosphorus polymer can be formed in a sealed vessel by adjusting amounts of PH_3 and NO to deposit the polymer at a desired deposition rate.

The polyhydride phosphorus polymer can be used as an intermediate product to make other phosphorus compounds. For example, the polyhydride phosphorus polymer can be deposited on a substrate such as an article of flammable material or on a part intended for use in a fire hazard environment or in a high temperature environment. The polyhydride phosphorus polymer can be deposited as a uniform film or coating with a thickness of a few microns or, if desired, built up to several mils, *e.g.*, 1 to 100 μm, 100 μm to 1 mm, 1 to 10 mm. The polyhydride phosphorus polymer can be converted to another phosphorus compound by oxidizing the polyhydride phosphorus polymer. For example, the polyhydride phosphorus polymer can be oxidized in a gaseous environment or by contacting the polyhydride phosphorus polymer with a solution of hydrogen peroxide. In the case of an article coated with the polyhydride phosphorus polymer, the coated article can be immersed in a solution of hydrogen peroxide to convert the polyhydride phosphorus polymer to a phosphorus compound such as a polymeric phosphine oxide film/coating. A preferred polymeric phosphine oxide includes phosphorus, hydrogen and oxygen. However, other constituents may also be incorporated in the phosphine oxide.

The polymeric phosphine oxide can be used for imparting fire retardant properties to flammable textile materials such as carpeting, drapery and clothing. Further details of such polymeric phosphine oxides can be found in U.S. Patent No. 4,072,653, the entire contents of which is hereby incorporated by reference. The polymeric phosphine oxide can also be used as a heat/fire resistant coating on articles of

manufacture such as oven/furnace parts, building materials, electronic components, automobile and aircraft parts, etc.

While various embodiments have been described, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

CLAIMS:

1. A method of making a polyhydride phosphorus polymer comprising subjecting phosphine to gas phase synthesis so as to produce the polyhydride phosphorus polymer.

2. A method according to claim 1, wherein the gas phase synthesis is carried out using a gas phase initiator.

3. A method according to claim 2, wherein the initiator comprises a free radical.

4. A method according to claim 1, 2 or 3, comprising generating the phosphine by a magnesium phosphide, calcium phosphide or aluminum phosphide precursor.

5. A method according to any of claims 1 to 4, wherein the gas phase synthesis is carried out by adjusting amounts of NO and the phosphine in a sealed vessel so as to deposit the polyhydride phosphorus polymer at a desired deposition rate.

6. A method according to any preceding claim, wherein the polyhydride phosphorus polymer is deposited on an article comprising a flammable material or on a metallic or polymer part.

7. A method according to claim 6, wherein the flammable material is an article of clothing.

8. A method according to any preceding claim, further comprising oxidizing the polyhydride phosphorus polymer.

9. A method according to claim 8, wherein the oxidizing comprises contacting the polyhydride phosphorus polymer with a hydrogen peroxide solution.

10. A method according to claim 6 or 7, further comprising oxidizing the polyhydride phosphorus polymer, wherein the article is immersed in the hydrogen peroxide solution.

11. A method according to claim 8, 9, 10 or 11, wherein the oxidizing converts the polyhydride phosphorus polymer to a polymeric phosphine oxide coating.

12. An amorphous polyhydride phosphorus polymer made by a method according to any preceding claim.

13. A coated article made by a method according to claim 6, 7 or 10.

14. An article of manufacture having deposited thereon an amorphous polyhydride phosphorus polymer.

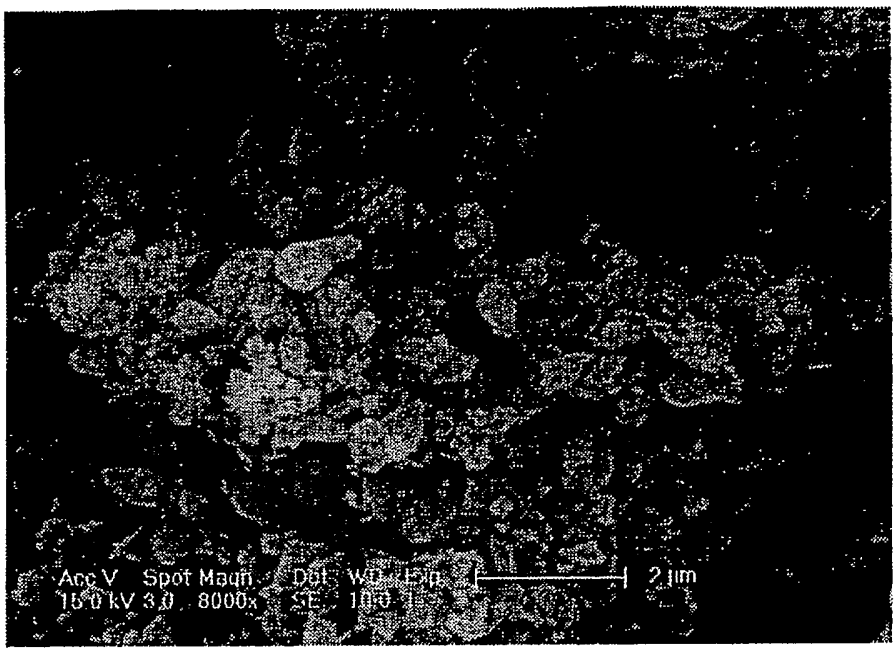

Acc.V Spot Magn Det WD
15.0 kV 3.0 8000x SE 10.0
2 µm

FIG. 1

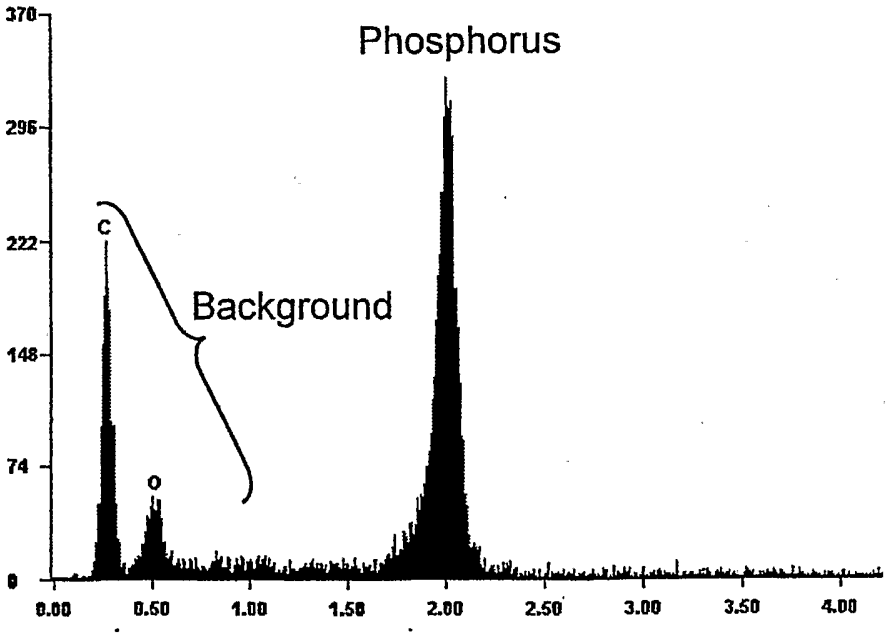

370
296
222
148
74
0
Phosphorus
C
O
Background
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00

FIG. 2