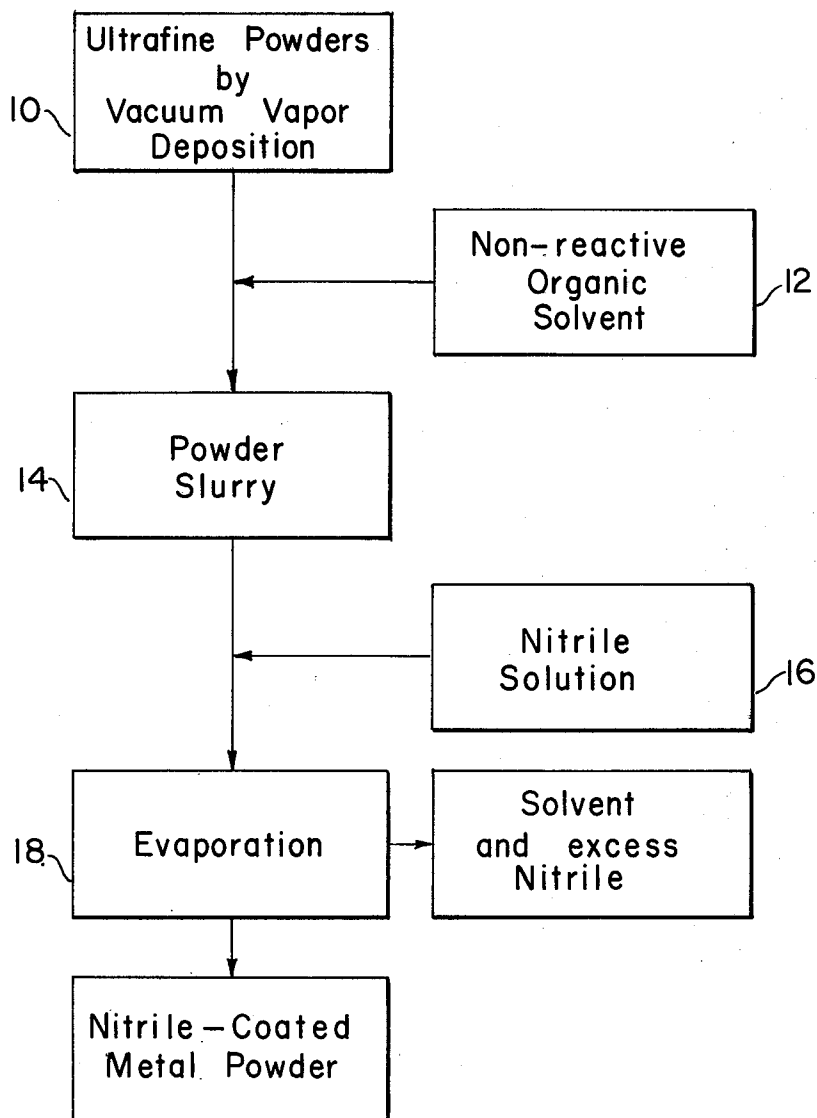


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PASSIVATION OF PYROPHORIC METAL POWDERS BY COATING
WITH AN ORGANIC NITRILE HAVING A C=C UNSATURATION
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PASSIVATION OF PYROPHORIC METAL POWDERS BY COATING WITH AN ORGANIC NITRILE HAVING A C=C UNSATURATION

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10 Claims. (Cl. 75-5)

This invention relates to pyrophoric powders and more particularly to a process of passivating pyrophoric powders.

It is a principal object of the present invention to provide a method of passivating pyrophoric powders without adversely affecting the potential energy of combustion.

A further object of the invention is to provide a method of treating highly reactive pyrophoric powders to provide stability to ambient air and moisture.

A further object of the invention is to provide a process for the production of stabilized metal powder having a small particle size.

A still further object of the invention is to provide stability of the pyrophoric powders with other materials.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components and the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

Briefly stated, the invention is directed to a process of passivating pyrophoric powders which are highly sensitive to ambient conditions and comprises absorbing onto the surface of the pyrophoric powder an organic compound which stabilizes the powder. The term pyrophoric as used in the specification and claims includes materials of varying degrees of sensitivity ranging from spontaneously ignitable in air at room temperature to flammability at elevated temperatures.

For a more complete understanding of the nature of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing which is a flow sheet illustrating the stabilizing process of the present invention and its relationship to other steps in the procedure for producing stabilized metal powders.

In accordance with the present invention, the physical and chemical properties of highly-reactive pyrophoric metal powders may be modified to provide advantages which were heretofore extremely difficult, if not impossible, to achieve. Since small particle size is considered one of the chief factors in flammability, it can be said that almost any alloy, metalloid, or metal will be pyrophoric if it is in fine enough particles and its heat of combustion is strongly exothermic.

By means of the coatings of the present invention pyrophoric metal powders and alloys can be rendered stable to ambient conditions of air and moisture without substantial decrease of the total energy available. Additionally, the metal powders are rendered more stable thermally.

The present invention has particular utility for example for stabilizing pyrophoric metal powders for use as ingredients in forming rocket propellants. The present invention is also useful in the production of pyrotechnics.

The various steps of the present invention for producing stabilized metal powders are shown diagrammatically

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in the drawing. In the first step 10 the ultra fine metal powders are preferably produced by vacuum deposition of metal vapors in a vacuum chamber. A metal is thermally vaporized at a pressure below about 500 microns Hg abs. in a non-oxidizing or inert atmosphere. The resultant metal vapors are then condensed under these pressure conditions to produce the metal power.

For a more detailed description of one process and apparatus for producing the metal powders, reference should be had to the copending application of Goon et al., Serial No. 81,312, filed January 9, 1961. The metal powders produced have an enormous surface area and small particle size. These powders are highly reactive and extremely pyrophoric.

In the next step 12, the metal powders are preferably wet down with a suitable liquid organic material and handled as a wet cake or slurry 14. Organic materials such as hexane, benzene, toluene, heptane, naphtha, tetrahydrofuran, methyl chloride, ethyl acetate and the like are suitable. In the wet state the metal powders are shielded and oxygen contamination is prevented.

In the next step of the process 16, a solution of an unsaturated organic nitrile in an organic liquid solvent is formed when the nitrile, such as tetracyanoethylene, is in solid form. The organic solvent preferably corresponds to the organic liquid used to form the metal powder slurry. When the nitrile is a liquid, such as acrylonitrile, it can be used directly without the addition of a solvent. By the term unsaturated organic nitrile, as used in the specification and claims, it is meant an organic nitrile having C=C unsaturation.

The organic material to be used for forming the slurry and the nitrile solution (where the nitrile is a solid) should possess certain properties. For instance, it should be non-reactive with the powders and should protect the powders from spontaneous ignition or oxidation. It should also be such that it can easily be removed by volatilization after the nitrile has been absorbed on the metal powder. The nitrile solution is then added to the metal powder slurry and thoroughly mixed. The adsorption of the nitrile on the metal powder is complete after approximately 1/2 hour. After the adsorption or coating process is completed, the organic solvent and any excess nitrile is preferably removed by an evaporation step 18 at a reduced pressure and the nitrile-coated powder is collected.

The invention will be more fully described in the following nonlimiting examples.

Example 1

In this example ultra-fine aluminum metal powder was used. This aluminum powder was produced by vaporizing aluminum metal in an evacuated chamber, the metal vapor stream being deflected through a substantial angle to provide for a downward flow of the vapors as described in the copending application of Goon et al., Serial No. 81,312, filed January 9, 1961. The downwardly deflected metal vapors were then condensed in free space at a total chamber pressure of about 180 microns Hg abs. to form ultra fine aluminum metal powder. The powder so formed was pyrophoric, jet black in color and had a dry bulk density of approximately 0.1 g./cc. and was 94% aluminum metal. The aluminum powder had a surface area of about 43 meters²/gram and had a particle size on the order of .01 micron or less. The purity and enormous surface area of the aluminum powder rendered it extremely reactive. When the powder was contacted with air, water, or an organic oxidizer, such as triethylene-glycol dinitrate, spontaneous ignition occurred.

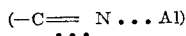
To the aluminum powder there was added sufficient benzene to moisten the powder and form a slurry of the

powder in benzene. A saturated solution of tetracyanoethylene in benzene was then thoroughly mixed with the aluminum powder slurry to effect the adsorption of the tetracyanoethylene on the surface of the aluminum powder. After ½ hour the benzene was removed by evaporation at a reduced pressure. The tetracyanoethylene coated aluminum powder was similar in appearance to the uncoated powder. The tetracyanoethylene content of the aluminum powder was approximately 15% by weight. The powder was thermally stable in air below 215° C. and ignited when heated in air to a temperature above 217° C. Also, the powder did not react when brought into contact with triethyleneglycol dinitrate. When the coated powder was remixed with benzene the tetracyanoethylene coating remained on the powder and did not dissolve.

Example 2

In this example the aluminum powder used was the same as in Example 1. The process was carried out in the same manner as Example 1 but with the exception that acrylonitrile was used as the stabilizing adsorbent agent. Additionally, since the acrylonitrile is a liquid, an organic solvent was not required. The coated aluminum powder was in the form of black, friable agglomerates. The acrylonitrile content of the aluminum powder was approximately 45% by weight. The aluminum powder was air-stable and did not react when brought into contact with triethyleneglycol dinitrate.

While the mechanism by which the nitrile is coated on the metal powder has not been determined, it has been postulated that the coating may result from (1) bonding of the nitrile to the metal powder via the nitrile bond i.e.



or (2) that the unsaturated nitrile compounds are polymerized by the powder to form a polymeric coating of the nitrile on the powder. It has, however, been determined that an unsaturated nitrile is necessary for stabilization of the pyrophoric powders. While a saturated nitrile is adsorbed onto the powders, it will not stabilize them. For example, the aluminum powder of the type used in Examples 1 and 2, which could be stabilized with unsaturated nitriles, was treated with acetonitrile, a saturated nitrile. Although 14% by weight of the acetonitrile was adsorbed onto the aluminum powder, the powder was not stabilized but was still extremely pyrophoric. Thus, while both saturated and unsaturated nitriles are adsorbed, only the unsaturated nitriles stabilize the pyrophoric powders. The fact that only the unsaturated nitriles provide for stabilization of the powders may be explained by the following considerations. The unsaturated nitriles since they have a C=C double bond for polymerization may be polymerized by the powder to form a protective coating on the powder and thus provide stabilization. Alternatively, the C=C double bond is an electron acceptor i.e. it is considered to be deficient in electrons. Accordingly, the C=C double bond can accept electrons from metals which have free electrons. Thus, the unsaturated nitrile by accepting electrons from the metal powder may render the powder stable. It is to be understood that foregoing theories may occur simultaneously and that one may be predominant. In view of the foregoing discussion it is believed that the nitrile coating on the metal powder is a polymer of the nitrile monomer. Accordingly, the term nitrile as used in the specifications and claims is intended to include nitrile polymers as well as the monomers.

It should be pointed out that the amount of unsaturated organic nitrile required to stabilize or passivate metal powders is a function of the purity of the metal powder and the particular nitrile that is used to coat the powder (for a given powder surface area).

For instance, in Examples 1 and 2 the aluminum powder used was the same but required 15% by weight of tetra-

cycanoethylene (Ex. 1) and 45% by weight of acrylonitrile (Ex. 2) for stabilization.

In Example 1 the aluminum powder was 94% aluminum metal and required 15% by weight of tetracyanoethylene. In comparison an aluminum powder produced in the same manner as that of Example 1 and having the same surface area, but being only 83% aluminum metal, required only 10% tetracyanoethylene for stabilization.

In respect to thickness of the nitrile layer, it was determined that sufficient nitrile, taking into account the foregoing variables, should be used in the coating process to provide at least a monolayer of nitrile coating and preferably a multilayer in the case of metal powders of high purity. Where the surface areas of the nitrile molecule and metal powder are known and assuming that the nitrile molecule will lie with its plane parallel to the metal powder surface, the amount of nitrile required to provide the desired number of layers can be readily estimated.

For example, aluminum powder having a purity on the order of 80% aluminum metal requires at least one layer and preferably two layers of nitrile for stabilization. Aluminum powder having a purity on the order of 90% aluminum metal requires at least three layers for stabilization.

While the specific embodiments of the invention have been described with respect to its application to pyrophoric aluminum metal powder, the invention is equally applicable to other pyrophoric powders of metals, metal-oids and alloys.

Some of the many known ways of producing metal powders to which the stabilizing process of the present invention may be applied comprise (a) the hydrogen reduction of certain readily reducible metal oxides, carbonates, nitrates, or formates, (b) the alkali metal reduction of certain metal halides, (c) metal amalgamation and subsequent removal of mercury by distillation, (d) metal hydride decomposition, (e) carbonyl decomposition, (f) halide decomposition, (g) electrolysis, (h) in plasma jet, and (i) arc disintegration.

Since certain changes can be made in the above without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of producing stabilized metal powders comprising vaporizing a metal at a pressure below about 500 microns Hg abs., condensing the resultant metal vapors at a pressure below about 500 microns Hg abs., collecting the resultant metal powder, treating the metal powder with an unpolymerized organic nitrile having C=C unsaturation in liquid form to provide a coating of said nitrile on said powder and separating the coated powder.

2. The process of producing stabilized metal powders comprising vaporizing a metal at a pressure below about 500 microns Hg abs., condensing the resultant metal vapors at a pressure below about 500 microns Hg abs., forming a slurry of the resultant metal powders in an anhydrous volatile hydrocarbon, treating said slurry with an unpolymerized organic nitrile having C=C unsaturation in liquid form to provide a coating of said nitrile on said powder and separating the coated powder.

3. The process of producing stabilized metal powders comprising forming in a non-oxidizing atmosphere a metal powder of small particle size, forming a slurry of the resultant metal powders in an anhydrous hydrocarbon, treating said slurry with an unpolymerized organic nitrile having C=C unsaturation in liquid form to provide a coating of said nitrile on said powder and separating the coated powder.

4. The process of producing stabilized aluminum metal powder comprising forming in a non-oxidizing atmos-

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phere an aluminum metal powder having a surface area of about 43 meters²/gram, forming a slurry of the resultant metal powder in an anhydrous hydrocarbon, treating said slurry with an unpolymerized organic nitrile having C=C unsaturation in liquid form to provide a coating of said nitrile on said aluminum powder and separating the coated powder.

5. The process of passivating pyrophoric metal powders comprising forming a slurry of said metal powders in an anhydrous hydrocarbon, treating said slurry with an unsaturated unpolymerized organic nitrile in liquid form to provide a coating of said nitrile on said powder and separating the coated powder.

6. The process of stabilizing highly reactive metal powders comprising forming a slurry of said powder in an anhydrous volatile hydrocarbon, mixing said slurry with a solution of an unsaturated organic nitrile selected from the group consisting of tetracyanoethylene and acrylonitrile to form a coating of said nitrile on said powder and separating said coated powder.

7. The process of stabilizing pyrophoric aluminum metal powder comprising forming a slurry of said aluminum powder in an anhydrous volatile hydrocarbon, treating said slurry with a solution of an unsaturated organic nitrile selected from the group consisting of tetracyanoethylene and acrylonitrile to form a coating of said nitrile

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on said aluminum powder and separating the coated powder.

8. A stabilized metal powder comprising a pyrophoric metal powder substrate and a stabilizing coating thereon said coating being a layer of an unsaturated organic nitrile.

9. A stabilized metal powder comprising a pyrophoric aluminum metal powder substrate and a stabilizing coating thereon said coating being a layer of an unsaturated organic nitrile selected from the group consisting of tetracyanoethylene and acrylonitrile.

10. A stabilized metal powder comprising a pyrophoric metal powder substrate and a stabilizing coating thereon said coating being a layer of an unsaturated organic nitrile and being insoluble in benzene.

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