

[54] **THERMALLY IGNITABLE ZIRCONIUM-PLASTIC COMPOSITION** 2,951,752 9/1960 Stevenson 149/114 X
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[52] **U.S. Cl.**..... 149/2, 149/19.5, 149/44, 149/114, 102/66, 102/90

[51] **Int. Cl.**..... C06d 1/02

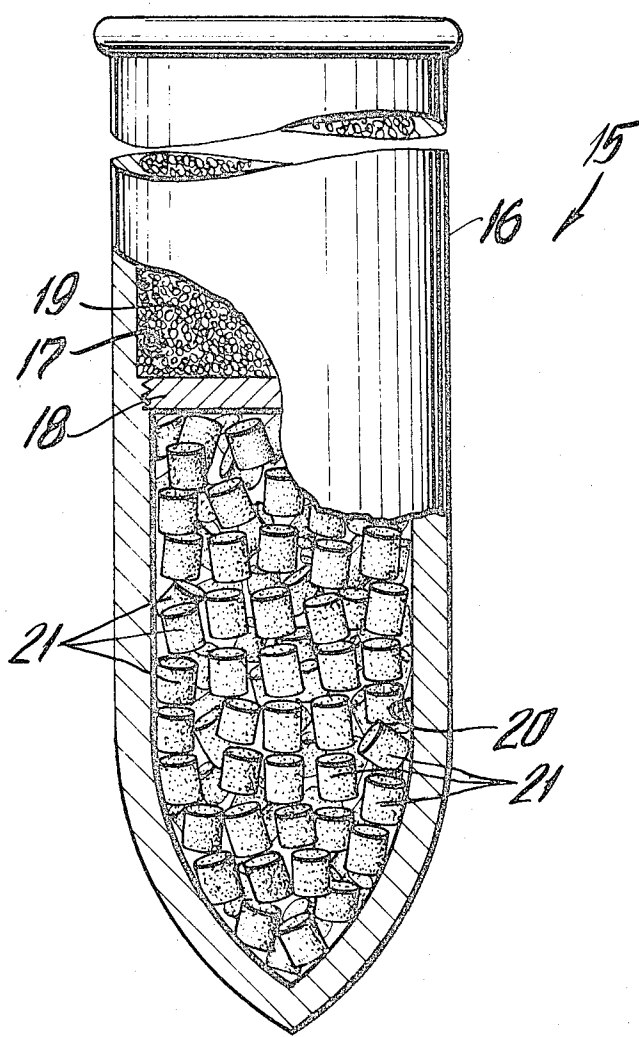
[58] **Field of Search** 149/19, 42, 43, 44, 114, 149/2, 19.5; 260/40 R

[56] **References Cited**
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[57] **ABSTRACT**
A thermally ignitable zirconium-plastic composition is provided comprising a thermally decomposable plastic having zirconium powder dispersed therethrough, the plastic being formed of a polyester resin.

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4 Claims, 5 Drawing Figures



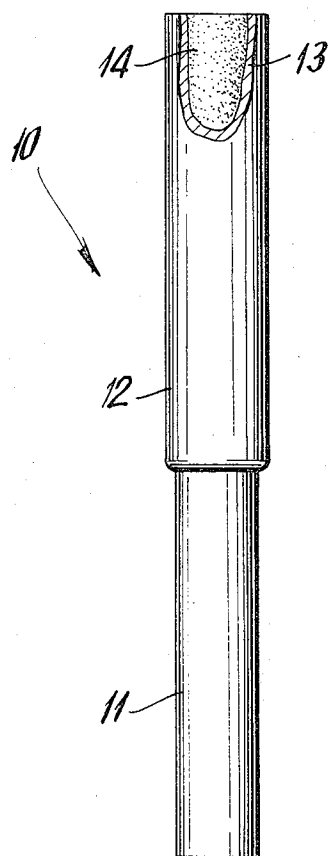


FIG. 1

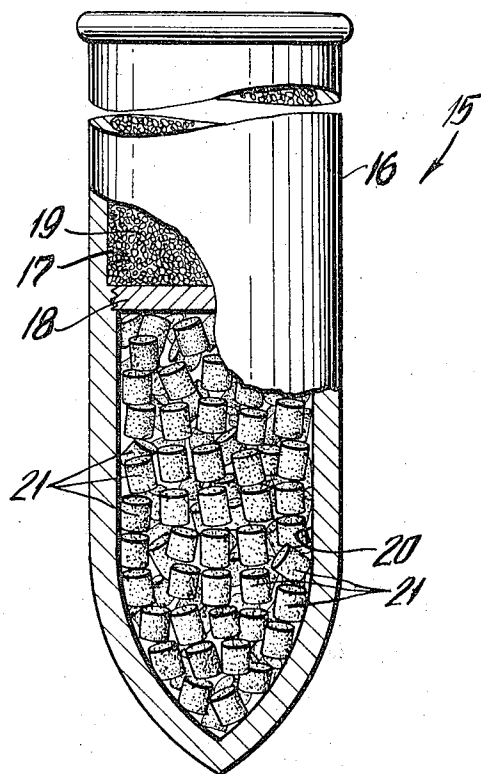


FIG. 2

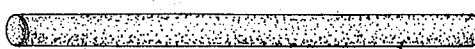


FIG. 3

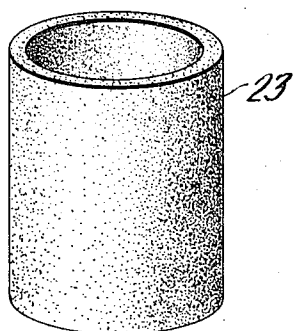


FIG. 4

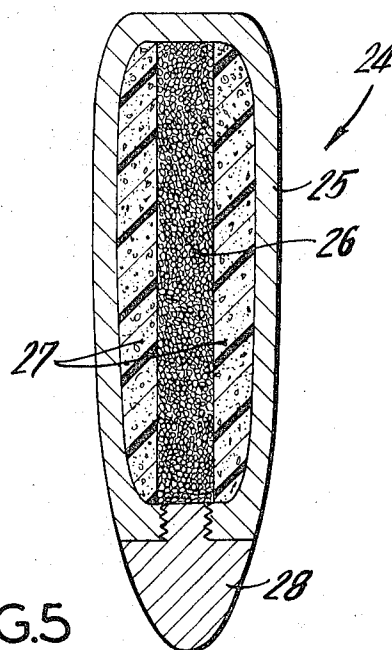


FIG. 5

THERMALLY IGNITABLE ZIRCONIUM-PLASTIC COMPOSITION

This invention relates to a thermally ignitable zirconium-plastic composition and to a composite article of manufacture comprising said composition.

Pyrotechnic devices are known for military use in which a metal is employed as fuel together with an oxidizer and binder. Such devices may comprise projectiles filled with magnesium or aluminum powder because of the high heat of oxidation of such metals. However, these materials, because of their low densities, do not exhibit good penetrating power when devices containing said materials are exploded.

Zirconium metal powder is known to be a very incendiary material. However, this metal is very difficult and expensive to form into shapes by normal powder metallurgy techniques owing to its inherent galling characteristics.

It would be desirable therefore to provide a method by which zirconium powder can be used in the production of pyrotechnic devices, incendiary elements, parts for projectiles, tracer elements and the like.

OBJECTS OF THE INVENTION

It is an object of the invention to provide a thermally ignitable zirconium composition capable of being formed in any desirable shape.

Another object is to provide a thermally ignitable article of manufacture formed of a composite comprising zirconium powder as an essential ingredient.

A still further object is to provide an incendiary projectile which includes a thermally ignitable zirconium-plastic composition as one of its elements of construction.

These and other objects will more clearly appear when taken in conjunction with the following disclosure and the accompanying drawing, wherein:

FIG. 1 is illustrative of a flare comprising a thermally ignitable element produced by the invention;

FIG. 2 is an incendiary projectile partially broken away showing pills or small cylinders of a zirconium composite composition confined therein;

FIG. 3 depicts a rod produced from the zirconium composite composition of the invention;

FIG. 4 is a hollow sleeve formed of the zirconium composite composition provided by the invention; and

FIG. 5 is another embodiment of an incendiary projectile in which the zirconium-plastic composition is employed as one of the elements of construction.

STATEMENT OF THE INVENTION

Stating it broadly, the invention is directed to a thermally ignitable zirconium-plastic composition comprising a thermally decomposable polyester resin having zirconium powder dispersed therethrough in an amount constituting at least about 40 percent by weight, and preferably at least about 50 percent by weight, substantially the balance of the composition comprising said polyester resin.

The loading of zirconium powder in the resin may preferably range by weight from about 50 to 95 percent and, more preferably, from about 60 to 85 percent. A loading of about 70 to 75 percent zirconium powder has been found to be particularly useful in the produc-

tion of incendiary devices of the type illustrated in the drawings to be discussed later.

The novel zirconium-plastic composition comprising said polyester resin is capable of being formed into any desirable shape by casting and polymerization. Examples of shapes are pellets, tablets, pills, rods, cylinders, incendiary flares, sleeves or liners for use as inserts in ordnance projectiles, and the like. Or, if desired, the composition while still in the fluid condition, can be dip-coated onto the inside or outside diameters of projectiles to provide a pyrophoric capability.

Additional metallic or chemical additives may be included in the composite material to attain specific results.

Examples of uses of the composite are illustrated in FIGS. 1 to 5. FIG. 1 depicts a flare 10 comprising a handle 11 to which said flare is mounted and a pyrotechnic portion 12 comprising a hollow cylinder 13 of, for example, combustible wax-impregnated composition paper into which is cast the composite zirconium-plastic composition 14 of the invention. This flare is particularly advantageous because of the intense and penetrating lighting effects achievable with it.

FIG. 2 illustrates an incendiary ordnance projectile designated generally by the numeral 15 comprising a casing of fracturable metal 16, e.g. steel, which has an explosive-containing chamber 17 in back of divider 18 screw-threaded to the inner wall of the casing to maintain its position. The divider is relatively thin and may be made of the same metal as the casing.

The chamber 17 contains an explosive charge 19. In the forward chamber 20 of the projectile is confined a plurality of pellets 21 formed from the composition of the invention. The explosive charge may be of any desirable composition. The means for detonating the charge are well known and need not be shown or described here.

When the projectile is fired, the divider is ruptured and the heat and pressure released as a result of the detonation causes the casing to burst and the pellets to ignite. The burning pellets are dispersed over a broad path in the area of the target to provide the necessary incendiary capability of the projectile.

FIG. 3 depicts an incendiary element 22 in the form of a rod produced by casting in a mold. Such elements may have use in the manufacture of pyrotechnic displays. Similarly, sleeves or liners 23 (FIG. 4) may be easily produced by casting in a mold provided with a center core corresponding to the inner diameter of the sleeve. The sleeve may be used as a liner in a projectile to provide incendiary capability similar to that described for FIG. 2. FIG. 5 illustrates such a projectile in which the zirconium-plastic composition is employed as a sleeve, the projectile 24 comprising a casing 25 of fracturable steel, a longitudinally shaped charge 26 axially supported therein surrounded by a sleeve 27 of the zirconium-plastic composition and a nose 28 of heat treated steel having firing means associated therewith (not shown). When the projectile strikes the target, the firing means causes the charge 26 to explode and fracture the casing. The sleeve of the zirconium-plastic composition is similarly caused to fracture and thermally ignite while being dispersed in a board path relative to the target.

As will clearly appear from the foregoing, the invention also resides in an article of manufacture comprising an incendiary element, whether employed in the

manufacture of flares, or as an element for a projectile, or even as an element for pyrotechnic display commonly employed in fireworks.

The composite zirconium-plastic composition may be employed in incendiary projectiles in other forms. For example, controlled amounts of the composition may be poured into the base of a shell to provide an incendiary plug in contact with the explosive charge; or, the shell may comprise substantial amounts of the zirconium-plastic composition without an initiator, the composition being thermally ignited when the shell is caused to absorb a high degree of kinetic energy, such as occurs under high velocity impact.

The size of the zirconium powder employed in making the composite should be such as not to react pyrophorically under ambient conditions. The average size is preferably over about 15 microns and may range up to about 4000 microns.

In producing the composite composition using zirconium powder and polyester resin as the materials, a polyester resin referred to in the trade as "Durez," type PR-130, may be employed (manufactured by Durez Plastic Division of the Hooker Chemical Corporation). This resin is syrupy and has a Brookfield viscosity at 77°F of 1900, a specific gravity of 1.13 and is in the uncatalyzed state before use. Generally, organic peroxides are used as catalyst, such as benzoyl peroxide, dichlorobenzoyl peroxide, lauroyl peroxide, methyl ethyl ketone peroxide, and the like. The peroxide catalyst may be added in small but effective amounts of up to about 2 percent of the weight of the resin.

The polyester resins which may be employed in carrying out the invention embrace a broad range of compositions. Generally, the resins are produced by the reaction of dibasic acids with dihydric alcohols, although trifunctional monomers, such as glycerol or citric acid may be used. Polyester resins particularly apply to products made using a mixture of unsaturated dibasic acids, e.g. maleic, along with saturated dibasic acids.

The unsaturated polyester resins can be further polymerized through cross linking because they are unsaturated. Generally, another unsaturated monomer, such as styrene, is added during this second stage of polymerization which can be made to occur at ordinary temperatures with suitable peroxide catalysts. It is usual for the first stage of polymerization (the ester formation stage) to be carried out at the manufacturing plant and the second stage polymerization out in the field.

Generally speaking, maleic anhydride and fumaric acid are the usual unsaturated acid components, while phthalic anhydride, isophthalic, adipic or azelaic acids are the corresponding saturated materials. The commonly used glycols are ethylene, propylene, diethylene, dipropylene and certain butylene glycols. The polymerizable monomers which may be added are styrene, vinyltoluene, diallylphthalate, methyl methacrylate, chlorostyrene, methyl styrene, divinylbenzine or triallyl cyanurate. Water is eliminated during the first stage combination of acid and glycol. The second stage polymerization out in the field produces no gas or liquid products. The curing stage is fairly rapid.

As will be apparent, a broad range of polyester resins may be employed in producing the composite zirconium-plastic composition of the invention.

A composite mixture is produced, by way of a specific embodiment, by mixing 80 percent by weight of

zirconium powder of approximately 20 microns average size with 20 percent by weight of the resin. Since it is desirable not to exceed a curing temperature of 250°C in view of the reactivity of finely divided zirconium powder, an organic peroxide catalyst is selected which will effect curing at a relatively low temperature, provided the mixture is cast immediately into a mold after being catalyzed.

It is preferred to add the curing agent to the resin before adding the zirconium powder. Depending upon the particle size, the zirconium powder should be handled carefully, since friction can cause the powder to ignite. Thus, the curing agent is first added to the resin and the mixture blended thoroughly. A typical catalyst is 0.2 percent of dichlorobenzoyl peroxide by weight of the resin. The powder is then preferably added to the resin mix 25 percent at a time, with the mixture being thoroughly blended after each addition. This produces a pourable syrupy mixture. A 25 inch vacuum is applied (based on mercury) to remove entrapped air.

After removing the entrapped air from the syrupy composition, the mixture is then poured slowly into a vibrating mold to produce the desired shape depending on end use. Silicone or teflon-based release agents are coated onto the mold surfaces to assure easy removal of the cast composition. As stated hereinabove, the mixture may be dip-coated onto fairly stiff wires of suitable length to produce sparklers for pyrotechnic display. Where heat is relied upon to cure the mix in the mold, the temperature may range from 200°F to 275°F. Preferably, the temperature should be as low as possible.

As has already been stated hereinbefore, the composition may include certain inorganic additives, such as oxidizers, coloring agents, and the like, depending on the end use of the composite. Examples of oxidizers are potassium perchlorate, sodium nitrate, sodium perchlorate, manganese dioxide and many others. Examples of coloring agents are the copper compounds, copper chloride, copper nitrate, etc., strontium perchlorate, strontium nitrate, strontium chloride and other strontium compounds; cobalt compounds, including cobalt chloride, cobalt nitrate; and many other coloring agents.

Thus, the composition may contain at least one of the additives selected from the group consisting of oxidizers and coloring agents.

As illustrative of various compositions which are provided by the invention, the following examples are given:

EXAMPLE 1

Zirconium powder (20 microns average size)	70 wt. %
Liquid polyester resin (Durez PR-130)	30 wt. %

To the polyester resin maintained at room temperature is added about 0.3 percent by weight of dichlorobenzoyl peroxide. The two ingredients are well mixed as described hereinbefore, the zirconium powder added and mixed and the uniform mixture after removal of entrapped air then poured into a vibrating mold containing a plurality of cavities corresponding to a rod of the type illustrated in FIG. 3. The mixture is

allowed to cure in the mold, following which the mold is disassembled and the cast rods removed.

EXAMPLE 2

(1)	Zirconium powder (about 50 microns)	60 wt. %
	Liquid polyester resin (Durez PR-130)	40 wt. %
(2)	Zirconium powder (about 100 microns)	85 wt. %
	Liquid polyester resin (Durez PR-130)	15 wt. %

The foregoing compositions are formulated as in Example 1, methyl ethyl ketone peroxide in an amount of about 1 percent by weight of the resin being used to cure the resin. Another example is as follows:

EXAMPLE 3

Zirconium powder (from 75 to 150 microns)	80 wt. %
Liquid polyester resin	15 wt. %
Unsaturated styrene monomer	5 wt. %

The zirconium powder and plastic mix are compounded similarly as described above with about 0.2 percent of benzoyl peroxide by weight of the resin being used as the catalyst.

The following illustrates a composition for use in producing pyrotechnic displays.

EXAMPLE 4

Zirconium powder (about 20 microns)	65 wt. %
Polyester resin (Durez PR-130)	35 wt. %

As will be evident from the foregoing examples, the cured cast produced contains by weight about 60 to 85 percent zirconium and from about 15 to 40 percent resin.

The ingredients are formulated to provide a uniform mixture. To the formulation is added about 15 percent of strontium perchlorate by weight of the mixture, about 0.5 percent by weight of dichlorobenzoyl peroxide being employed as the catalyst. The strontium perchlorate acts both as an oxidizing and as a coloring

agent. Part of the formulated mixture is cast into long narrow rods for use in pyrotechnic display. In addition, the composition may be dip-coated onto suitable lengths of wire to produce sparklers common in fireworks display.

An example of another polyester resin available in the market is one sold by Commercial Resins Division of Interplastic Corporation, Minneapolis, Minnesota, under the trade name "Corezyn 3" is a viscous liquid resin whose viscosity is over 100,000 cps and has a specific gravity of 1.23.

While oxidizers and/or coloring agents may or may not be added to the formulation, these additives, when present, may range in total amounts up to about 30% by weight of the final zirconium-plastic mixture. Where the polyester resin is defined as comprising substantially the balance of the zirconium-plastic composition, it does not exclude the presence of such additives.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. A cast thermally ignitable zirconium-plastic composition consisting essentially by weight of about 60 to 85 percent zirconium powder of particle size falling within the range of about 15 to 4,000 microns dispersed through a cured matrix of about 15 to 40 percent of a polyester resin making up essentially the balance.

2. The zirconium-plastic composition of claim 1, wherein the amount of zirconium powder is approximately 70 percent.

3. A cast thermally ignitable composite article of manufacture comprising an incendiary element formed of a cured zirconium-plastic composition consisting essentially by weight of about 60 to 85 percent zirconium powder of particle size falling within the range of about 15 to 4,000 microns dispersed through a cured matrix of about 15 to 40 percent of a polyester resin making up essentially the balance.

4. The thermally ignitable composite article of claim 3, wherein the composition contains approximately 70 percent zirconium.

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