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ENCAPSULATION OF ROCKET AND MISSILE FUELS WITH METALLIC AND POLYMERIC COATINGS

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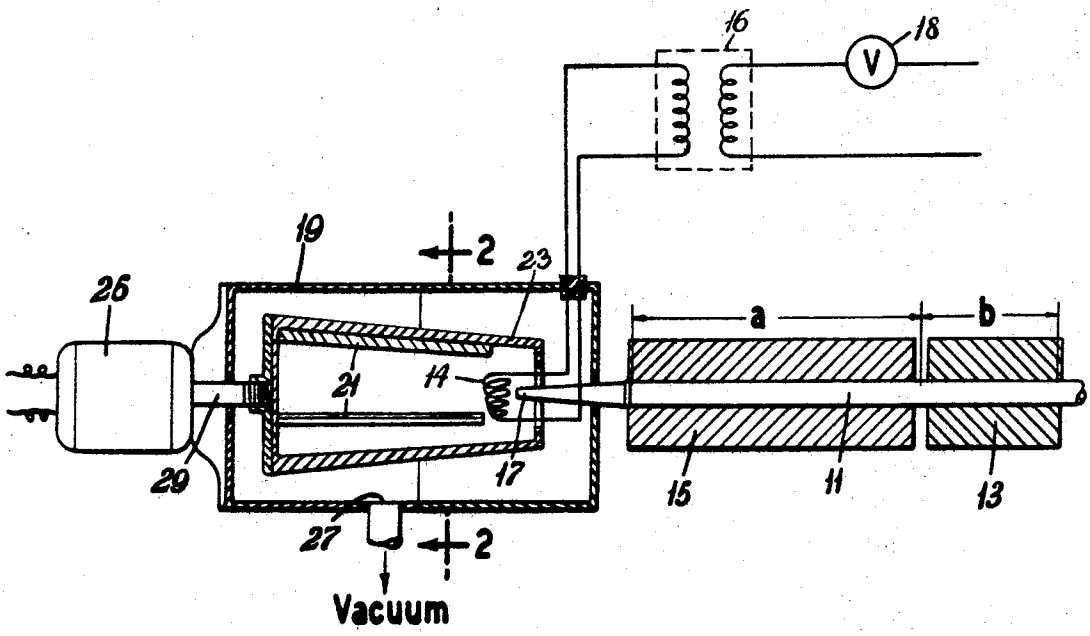


Fig. 1.

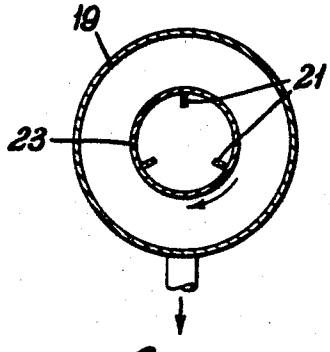


Fig. 2.

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ENCAPSULATION OF ROCKET AND MISSILE FUELS WITH METALLIC AND POLYMERIC COATINGS

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U.S. Cl. 149—7 18 Claims

The present invention is directed to the encapsulation of solid fuel components for missile and rocket propellants. More particularly the present invention is directed to coatings for solid particulate components of propellant formulations which will make for safe handling and storage of such materials.

Potent solid propellant components for missile and rocket propellant formulations necessarily should have a high weight percent of available reactants for maximum utilization of fuel energy. Solid oxidizers having high oxygen content and showing possibility for use in solid formulations include such materials as ammonium perchlorate, lithium perchlorate and nitronium perchlorate, NO_2ClO_4. These compounds contain from 50 to 67 percent combined oxygen, and by volume, some have more available oxygen than does liquid oxygen. Thus they have great potential as energetic oxidizers in solid fuel formulations for missiles and rockets. Unfortunately, most of these materials are also highly reactive and somewhat unstable chemicals, so reactive in fact that they are or can be difficult and dangerous to contain. Some react with explosive force in contact with water and organic compounds such as alcohol, amines, ether, phenols and aromatic hydrocarbons. Lithium and nitronium perchlorate specifically are also remarkably hygroscopic and are hydrated on even brief exposure to atmospheric humidity to cause deterioration and even to form a dangerous and explosive mixture.

Potent reducing agents in solid form which are also employed in rocket formulations likewise create problems in handling and storage. Such materials as lithium hydrides, lithium aluminum hydrides, aluminum hydrides in solvated or free form, boron hydrides, hydrazine nitrate, and the like are all so readily reactive that they hydrolyze readily on contact with water or atmospheric moisture, and in contact with organic agents such as alcohols, acids, ketones, and the like, will so reduce the organic materials as to create dangerous conditions and decrease the available amount of reducing material for propellant formulations.

The need is therefore obvious to find a manner or means of preventing the contact of such propellant materials to water, atmospheric humidity and to organic compounds. Inasmuch as the most superior binders and solid fuel systems known today are organic in nature or are formulated in organic systems, the use of potent oxidizers, reducing agents and combination components employed in rocket fuel formulations is necessarily dependent upon providing a stable inert moisture-impervious coating for the solid material. There was heretofore, no known solution to utilizing existing polymers and conventional coating techniques with certain of these products because of the unusual sensitivity to water, solvents, organic polymers, and the like.

It has been known also that certain light metals, such as lithium, aluminum, beryllium, sodium, and magnesium having atomic weights below 27 are energetic fuels for rocket propellant formulations and increase the specific thrust thereby. Ordinarily, such materials are ground to a fine particle size and incorporated by stirring into the organic binder for the solid oxidizer and reducing agents. This technique obviously increases the number of steps

required in preparing the propellant formulation, causing problems in securing an adequate dispersion of such metals in the fuel or binder and imposing problems in stirring the entire formulations which might cause fracturing of pellets of the potent components. This latter could lead to unwanted reactions and possible explosions.

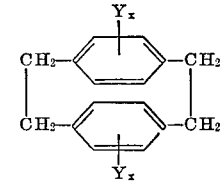
It is an object of the present invention to provide means for coating surfaces which are potentially reactive or subject to hydrolysis or chemical attack. It is a further object of the present invention to provide for coating surfaces of propellant components with evenly dispersed fuel metals and a polymeric coating, which coating is uniformly insoluble in common organic solvents, is completely inert and resistant to the highly reactive components, impermeable to moisture and yet provides a tough exterior coating sufficiently resistant to mechanical rupture for normal handling without the consequential dangers recited above simultaneously with providing available energetic metal fuel for increasing the thrust efficiency of rocket propellant formulations based thereon.

According to the present invention, it has now been discovered that strong inert, moisture-impervious coatings can be appiled to solid particulate propellant components which simultaneously provides coatings which are highly resistant to solvents, and protect the material from all of the organic materials and from atmospheric humidity, and still provide an available source of energetic metal fuels. In addition, the coatings as described hereinafter have been found to be completely inert to all the materials and chemicals employed in propellant formulations and will still provide strong, tough polymeric coatings to the pellets to resist mechanical fracture. With this invention, it is now possible to employ all of these components with conventional organic fuels and binders and safely mix, handle and formulate the solid material without danger of explosion or unwanted reactions.

The coatings now discovered to provide these highly desirable results can be considered as a two-part coating, one part being an organic polymer of p-xylylene, the other being a light fuel metal having an atomic weight below 27 such as lithium, aluminum, sodium, boron, berylium and magnesium. It is critical in this invention that the coating be selected with care, and that it be applied to the pellet or granule with equal care, as is hereinafter set forth in detail.

Thus, as one embodiment of this invention there is provided a safely protected and coated particulate propellant component comprising a particle of a solid potent oxidizer or reducing fuel component having as a coating thereon, a poly(p-xylylene) and a light metal fuel in atomically deposited form.

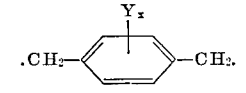
As another embodiment of the present invention there is provided a method for the coating of solid particulate propellant components which comprises the steps of pyrolyzing at a temperature between about 450° C. and 700° C. a cyclic di-p-xylylene having the general structure



(I)

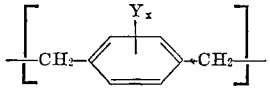
wherein Y is an inert aromatic nuclear substituent group having a sigma para value from about zero to about +0.8 and commensurate with the reactivity of the component to be coated, and x is an integer from 1 to 3, in-

clusive, thus forming reactive diradicals having the general structure



(II)

wherein x and Y are as defined above, depositing the thus formed diradicals on the surface of solid particulate propellant components while maintaining the particles in constant motion to continually expose fresh surfaces to said diradicals and depositing vapors of a light metal having an atomic weight below about 27 onto the surface of the moving particles, said particles being maintained at a temperature below 200° C. and below the condensation temperature of the reactive diradicals and the metal vapors, whereby the reactive diradicals and the said metals condense on the surface of the particles thereby coating said particles with a continuous coating of the said metal and a polymeric film of poly(p-xylylene) having the general repeating unit



wherein Y and x are as defined above.

In the above manner it is possible to provide a tough, moisture and solvent impervious coating to these solid pellets or granules and at the same time provide available fuel metals in well dispersed from throughout the propellant formulation. This result is particularly desirable when it is desired to protect very fine particle size propellant components. As the particle size diminishes, the percent coating required for adequate protection increases and the formulation suffers a serious handicap. By using only a polymer coating, the low fuel value of the polymer coating imparts a lower specific thrust to the formulation even with some of the more potent oxidizers. With the light metal present in the particulate component, the high fuel value of the metal counteracts the use of greater amounts of polymer coating and results in high specific thrust formulations even with fine particle size potent oxidizers.

Also by the principal embodiment of this invention, there is provided a system that protects the fuel metals themselves from unwanted reactions so as to make them safe to handle in these formulations. Lithium and sodium for example must always be carefully handled in rocket propellant compositions. By the technique of encapsulating the metal as well as the potent solid oxidizers or solid reducing agents, the entire propellant composition is safely handled.

It is a further embodiment of the present invention to provide a complete propellant formulation in one unitary particle without need for subsequent blending or mixing comprising in combination, a particulate potent oxidizer having an adherent coating thereon of a light metal and a poly(p-xylylene) having the general structure hereinbefore set forth. By this single unitary particulate system, it is now possible to avoid the sometime hazardous step of mixing and formulating the propellant system, or at least to avoid contact of the potent oxidizers with organic binders and solvents to which they may be reactive.

The present invention is now made possible because of the discovery that the poly(p-xylylene) and metal may be coated on the particulate propellant components either simultaneously or alternatively in the same equipment and by similar techniques. This discovery is based in part on the finding that although metals are normally vaporized at high temperatures and low pressures, the particular p-xylylene polymers employed herein are unaffected by such high temperatures since the polymers are formed only upon cooling of the reactive vaporous diradicals with themselves are stable at high temperatures. Hence there is no occasion for exposure of the polymer per se with the hot metals.

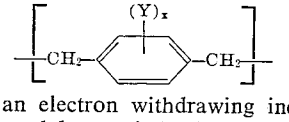
Any of the light metals normally employed in rocket propellant compositions for high specific impulse fuels can be used in this invention, particularly those having an atomic weight below 27 such as lithium, aluminum, sodium, beryllium and magnesium. These metals have reasonable rates of evaporation at pressures of 1 to 100 microns pressure at easily obtainable temperatures so as to be useful in this invention. As reported by S. Dushman in "Scientific Foundations of Vacuum Technique" (1949) John Wiley & Sons, New York, N.Y., these metals have the following rates of evaporation at 10 microns pressure at the noted temperature.

Metal	Temp., °C	Rate of evaporation grams/cm²/sec.
Sodium	290	5.48×10^{-5}
Magnesium	443	1.08×10^{-4}
Lithium	514–541	5.48×10^{-5}
Aluminum	996	8.51×10^{-5}
Beryllium	1246	4.49×10^{-5}
Boron	1355	4.76×10^{-5}

The most desirable of the metals are those having a high bulk density concomittant with a high temperature of oxidation in order to supply the highest specific impulse in propellant formulations. The only practical limitation on the metals used in this invention is the specific heat and vacuum necessary for their vaporization. However, even beryllium which vaporizes at about 1200° C. at 10μ pressure can be easily handled in a tungsten wire cone or tungsten boat as the vaporization element.

The invention has as its most practical and valuable utility, the coating and protection of potent propellant components that cannot be handled in contact with oxygen, atmospheric moisture, organic solvents and polymeric binders, such as for instance, nitronium perchlorate, aluminum hydride, lithium perchlorate and the like potent and highly reactive compounds. However, it is possible and clearly practical to so coat and protect any potent component for rocket formulations. Exemplary of such materials, but not to be construed as the only suitable components, can be mentioned the following additional potent materials; ammonium perchlorate, boron decahydride, hydrazine nitrate, hydrazine nitroformate, and other solid materials having practical uses as oxidizers or reducing agents in rocket formulations. Thus by the term "solid propellant component" as employed herein is meant those solid highly reactive and potent oxidizers and reducing agents employed as propellant components. All of these materials, when coated with the organic coatings of the present invention, are rendered so inert that they can be safely handled, stored and processed and if desired used immediately without further formulation.

The organic coating on the surface of the pellets or granules in direct contact with the solid propellant component, it has been found, must be of a polymer having the repeating unit.



wherein Y is an electron withdrawing inert substituent group on the p-xylylene unit having a sigma para value from about zero to about +0.8, x is an integer from 1 to 3, inclusive.

The inertness of the Y substituent group is of course necessary for the successful accomplishment of these ends. However, to those in the art, the selection of a particular inert Y group will be obvious knowing of the chemical nature and reactivity of the particular metal selected and the particular material to be coated. For example, it is known that cyano groups and carboxyl groups can be reacted with lithium and sodium metals, and that these

groups together with nitro groups may be quite reactive with reducing agents such as lithium hydrides, aluminum hydride and like active materials. Thus, the particular polymer coating should be selected with care so as to have groups inert to both the metals and the chemical compounds to be coated.

It has been found that such a polymeric coating in contact with the propellant components is basically inert to the highly reactive material and thus will deactivate the surface and permit complete control over the reactivity of the materials. The protection secured by the coating of poly-p-xylylene is not only due to the complete impervious inert polymer coating but also is apparently due to both electronic and steric effects on certain of the highly reactive materials with the former factor having the greatest measure of control.

As employed herein the term "sigma para value" means the relative electron withdrawing power of substituent groups conventionally known as the Hammett Sigma Para value as is set forth by Jaffe, in Chemical Review, 53, page 222, (1953). In this article, the principal aromatic substituent groups are classified as to their electron withdrawing power. Those substituents possessing a negative sigma para value will increase the average electron density on an aromatic nucleus and thus activate the nucleus toward reaction, whereas the groups possessing a positive sigma para value will significantly decrease the average electron density and thus relatively inactivate the nucleus, the degree of inactivation increasing as the sigma para value increases.

Without desiring to be bound by any particular theory, it is believed that the poly-p-xylylene can be made so inactive by the substituent groups that the polymer can coat pellets or granules of even the most reactive of these propellant components and be so inert and stable to the component that no outward reaction or explosion can occur regardless of the environment and materials contacting these components.

Exemplary of substituent groups on the poly-p-xylylenes which have sigma para values useful in this invention are, for example, those of the following list, in which the relative sigma para values are shown

Group	σ para value
—H	+0.000
$-C_6H_5$	+0.009
—F	+0.062
—Cl	+0.227
—Br	+0.232
—I	+0.276
—COOH	+0.265
—CHO	+0.216
$-\overset{O}{\overset{\|}{C}}-OCH_2-CH_3$	+0.522
$-CF_3$	+0.551
$-C\equiv N$	+0.628
$-SO_2CH_3$	+0.728
$-NO_2$	+0.778

The above listing is exemplary only, for any similar or different electron withdrawing group having a sigma para value from about zero to about +0.8 can be employed.

It is likewise critical herein that the sigma para value or the sum of the sigma para values of the substituent groups on the aromatic nucleus of the p-xylene unit of the polymer be commensurate with the reactivity of the component. For example, attempts at coating the very reactive nitronium perchlorate pellets and granules with single aromatic substituent polymers where the substituent group have an electron withdrawing power of only about +0.2 or +0.3 were uniformly unsuccessful due to extensive oxidation of the polymer by the nitronium perchlorate. This ultimately leads to degradation of the polymer and thus ineffective encapsulation.

However, the electron withdrawing power of the substituent groups appears to be additive so that two or more groups having a sigma para value less than about 0.35 on the aromatic nuclei of the repeating p-xylylene unit must be present although only one substituent group need be present when the group has a sigma para value of at least about 0.4 or greater. It is indicated that the greater the sum of the sigma para values of the substituent groups on the aromatic nucleus, the safer the polymer is in direct contact with the nitronium perchlorate.

Thus even the most reactive and potent of the known oxidizers for propellant composition, nitronium perchlorate, can now be safely coated with the tough impermeable coating having the fuel metal built into the coating to provide a safely handled and stored material.

Other oxidizers having similar or equivalent reactivities can be satisfactorily coated, with the sigma para value of the substituent group being selected commensurate with the relative reactivity of the component to be coated. For example, it has been found that all known components can be coated with poly(p-xylxylenes) having a sigma para value above +0.4 and that those which are relatively inactive or unreactive can employ poly(p-xylylenes) having sigma para values as low as zero. Such materials as ammonium perchlorate and lithium aluminum hydride can readily be safely coated with poly-(p-xylylene) itself, i.e. where Y is hydrogen, although it is generally preferred that the sum of the sigma para value of the Y groups is above +0.2 and even more particularly preferred, about +0.4.

The poly(dichloro-p-xylylene), poly(trichloro - p - xylylene) are most preferred. However, the corresponding bromine substituted polymers are also quite interesting and give good results.

It is quite possible also that when two substituent groups are present on the aromatic nuclei, they can be different groups as well as the same. For example, a poly(monobromo, monochloro-p-xylylene) can be employed as hereinafter discussed, as well as a poly-chloro-monocyano-p-xylylene or other suitable poly-substituted material wherein the sum of the sigma para values of the substituted groups total at least about 0.40 in the preferred system.

Similarly, copolymers of different Y groups in the polymeric units can be employed as long as the individual Y groups are insert to the light metals and the component and have sigma para values of from about 0 to about +0.8. These copolymers are likewise included within this invention and covered by the structural repeating unit of the polymer heretofore shown.

It is of course obvious that the coating of the substituted poly-p-xylylene and metal should be continuous over the entire surface of the pellet or granule, although it can be quite thin, i.e. in the order of about 0.1 mil or less, but preferably somewhat thicker. Since the polymer coating is itself an organic hydrocarbon and is combustible for rocket propellant purposes, the thickness is not narrowly critical but excessive coatings are not economically desirable. Also, excessive coatings of such polymers are desirably avoided unless accompanied by a high concentration of fuel metal in the coating because other polymer binders possess greater fuel and thrust power in rocket formulations and volume occupied by excessive coatings could better be utilized by higher thrust fuels.

In composite rocket fuel formulations composed of oxidizer and fuel, the oxidizer component is present generally in amounts between about 75 and 95 percent by weight in order to provide maximum theoretical thrust and utilization of fuel power. The use of extremely heavy coatings is quite undesirable since it necessarily takes part of the 5 to 25 percent of the weight of the fuel formulation allocated to the fuel per se. Thus, it is desirable in this invention that the organic coating be as thin as possible, and preferably not be more than about 10% by weight of the pellets, but yet be sufficiently strong and moisture resistant to prevent severe mechanical fracture of the pellets in normal handling.

Conversely, it is desirable that the fuel metal coating on the particles be as high as possible to secure complete encapsulation. The optimum concentration of fuel metal can be calculated or determined experimentally. It is preferred that the fuel metal be between 50 and 75 percent of the total encapsulants for the rocket formulation when the more inactive metals such as aluminum and magnesium are employed. With the more reactive metals such as lithium and sodium which themselves should be protected, it may be more desirable to go to higher amounts of polymer to insure the complete encapsulation of the particulate propellant component and of the light metal coating thereon.

The physical properties of the substituted p-xylylene coatings deposited in this manner make them quite useful whereas heretofore the known poly(p-xylylenes) could not have been used. Previously poly(p-xylylenes) could be prepared by pyrolyzing p-xylene at a temperature between about 900° C. and 1100° C., which severe conditions caused a molecular breakdown of the p-xylene into p-xylylene diradicals and a mixture of numerous other molecular fragments which upon cooling condenses to form a mass comprising polymer chains having a wide range of molecular weights and a mixture of other materials including some p-xylene, 1,2 dip-tolylethane and higher molecular weight by-products. A considerable portion of the polymeric mass consists of substantially insoluble cross-linked poly(p-xylylene) but almost 10 to 20 weight percent of the condensed mass comprises relatively low molecular weight materials which are soluble in such common solvents as benzene, acetone, carbon tetrachloride, and chloroform.

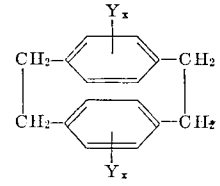
In mixing or coating applications, the extractable content of the protective coating could prove to be a highly deleterious contaminant. Also, such extraction frequently destroys the continuity of the coating and renders it permeable to substrate attacking fluids, and vaporous materials.

This process also suffers from the disadvantage that only about 10–15% of the p-xylene is pyrolyzed, with the remaining 85–90% of the p-xylene passing through the system unchanged. Attempts to coat xylene-sensitive, and highly reactive oxidizers with such materials would fail not only because of the high porosity of the polymer coating but also because of the possibility of xylene sensitivity of the potent component itself. With nitronium perchlorate, for example, the p-xylene present would immediately react with explosive force and thus be completely unsuitable as a coating. Even if the component were not sensitive to xylene and other organic materials, the porosity of the polymer coating would require exceedingly thick coatings to secure moisture protection of the reactive material at a very substantial sacrifice to optimum fuel potential.

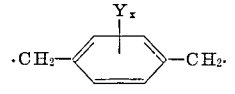
The process also suffered in that substituent groups on the aromatic ring were consistently cleaved off by the high temperatures necessary for the pyrolysis of the p-xylene. At temperatures of about 800°–900° C., both organic and inorganic groups are cleaved from the aromatic nuclei making it impossible to prepare a polymer having the Y substituent groups of the present invention. As heretofore mentioned, it is the Y substituent group that can so inactivate the polymer aromatic nuclei so that is can safely encapsulate and protect certain of the more reactive potent oxidizers.

It is an unusual facet of the present invention to provide complete coverage of the particle surface with a micro thin coating in which the organic coating is solely and completely a polymer free of p-xylene and other organic by-products and having electron withdrawing groups to stabilize the polymer against reaction but yet provides complete moisture and solvent protection for the propellant components and simultaneously provides available metal fuel for high specific thrust formulations and applications. This is now possible because of the

fact that the sole organic material in contact with the propellant component is a pin-hole free coating of poly-(p-xylylene) which is applied by the technique herein recited, starting with a di-pixylylene having the structure



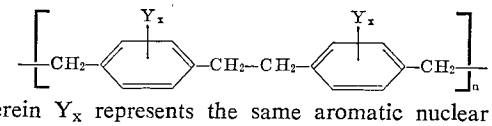
which under fairly mild temperatures cleaves quantitatively into two reactive diradicals which can be the same or different, to provide a vaporous condensation system which is free of other organic materials. Pyrolytic cleavage occurs at temperatures exceeding about 450° C. and most advantageously at temperatures between about 550° C. and 700° C. to form the reactive diradical



Regardless of the pressure employed, pyrolysis of the starting cyclic di-p-xylylene begins at about 450° C. and does not appear to be a function of the operating pressure. At temperatures above about 700° C., cleavage of the substituent group can occur, resulting in a tri- or poly-functional species causing cross-linking of highly branched polymers.

Pyrolysis temperature is essentially independent of the operating pressure. It is however preferred in the invention that reduced or subatmospheric pressures be employed. For most operations, pressures within the range of 0.0001 to 10 mm. Hg are most practical. However, if desired, greater pressures can be employed. Likewise, if desirable, inert non-organic vaporous diluents such as nitrogen, argon, carbon dioxide, steam and the like can be employed to vary the optimum temperature of operation or to change the total effective pressure in the system.

The diradicals formed in the manner described above can be generated simultaneously with the vapors of the light metal and are made to impinge upon the surface of the propellant component maintained at a temperature below 200° C. and below the ceiling condensation temperature of the vaporous diradicals present and the metal vapors thereby condensing thereon and thus spontaneously polymerizing the diradicals to form a uniform coating of the metal and the linear homopolymer having the general structure



wherein Y_x represents the same aromatic nuclear substituents as defined in structure (I) and n is a number from 10 to 10,000 or higher. Thus, it is seen that the condensation-polymerization operation does not affect the aromatic portion of the diradical (II), nor does it affect the substituent groups.

It is also seen that the vaporized metal does not interfere with or substantially affect the polymerization of the diradicals as they condense and polymerize. It is because of this technique that it is possible to simultaneously codeposit the metal fuel with the poly(p-xylylene), although if desired, it is also possible to make alternative depositions of polymer and metal by first vaporizing the cyclic dimer and coating it, and subsequently vaporizing and depositing the metal. However, for obvious reasons, the codepositing of poly(p-xylylene) and metal is more preferred.

By this technique it is very easy to control the relative amount of polymer and metal to be deposited on the propellant component. The temperature of the vaporization or melt pool of metal and the respective amount of

polymer and metal in their respective vaporization pools can vary within any selected limits depending on what proportions of each are desired, with the time to which the particles are exposed determining the relative thickness of the coating applied.

In this technique, it has also been found possible to control the molecular weight of the homopolymers by control over the particular condensation conditions. It has been discovered for instance that within relatively narrow ranges of temperature changes in the condensation temperature (i.e. 10–20° C.) some distinct control over the molecular weight of the polymer can be secured, provided that all such temperatures are below the condensation temperature of the p-xylylene species.

In order to insure uniformity of coating of particulate material, the material must be maintained in such a constant and random motion as to continually expose fresh surfaces to the condensing diradicals and metal vapors.

The particular material that can be coated by the present invention can be in the form of pellets, small objects, granular particles, and the like. The only restriction is that the material be able to be maintained in constant motion without losing its particulate nature such as by crumbling or breaking. Generally, such solid propellant components are available in pellet or granular form. Smooth surfaced pellets, spheres, or like geometric forms are most easily coated with a minimum of poly-p-xylylene and metal and are hence preferred although irregular granules can be employed if desired. In such instance, it may be necessary to employ heavier coatings of polymer to completely fill all cracks and voids in the granules and to provide for sufficient reinforcement of weak edges to prevent the mechanical fracture during subsequent handling.

An apparatus adapted for the performance of the above-mentioned process is shown in the drawings in which FIG. 1 schematically represents a coating apparatus and FIG. 2 is a cross-section of the deposition chamber.

Referring now to FIG. 1, said apparatus comprises a pyrolysis chamber **11** having two temperature zones *a* and *b*. The zone *b* is provided with heating means **13** sufficient to sublime or vaporize the di-p-xylylene disposed within that end of the pyrolysis chamber **11** and capable of maintaining a temperature of 150–200° C. The second zone *a* communicating with the first zone *b* is provided with heating means **15** sufficient to pyrolyze the vapors produced in said first zone *b*.

In a preferred embodiment, the pyrolysis tube **11** is composed of Vycor or quartz tubing. The heating means **15** is a combustion furnace capable of maintaining temperature of at least 450° C. to about 700° C. and high heat pool **14** being capable of maintaining a temperature of 1000° C. to 1500° C. and at least sufficient to vaporize the metal at the pressure employed. A coating chamber **23** is equipped with baffles **21** and shaped to retain particulate materials nearest one end thereof, said chamber **23** also being penetrated by the nozzled posterior portion **17**, of the aforementioned pyrolysis chamber **11**. In coating chamber **23** there is provided means for vaporizing metal, preferably employing a metal evaporation source **14** such as a tungsten wire spiral heater connected to a suitable current transformer **16** by power leads leading into coating chamber **23** through vacuum tight insulators. Heat of the metal evaporation source **14** is controlled through a Variac **18** or other suitable current regulating device. Rotatable means such as motor **25** and connecting shaft **29** impart a rotary motion to the coating chamber **23**. Said motor and shaft being adapted to support and also impart to said coating chamber **23** a movement whereby the said particulate material in said coating chamber **23** undergoes a tumbling motion. Other types of tumbling means could also be used to impart motion to the coating chamber **23**. It is important, however, to keep the particles in random motion so as to continually expose fresh surfaces for coating.

The agitating means of the present invention is not restricted to a motor and connecting shaft; any electromechanical device capable of imparting rotational or translational motion or a combination thereof can be incorporated in said agitating means with the provision that a continuous tumbling motion as hereinbefore mentioned be imparted to the particulate material disposed within the said coating chamber **23**. For instance, a magnetic coupling device can be used whereby a rotating magnetic field set up by the agitating means is transferred to the coating chamber thus imparting a rotary motion to said coating chamber **23**. A vacuum-supporting wall **19** surrounds said coating chamber **23** and the nozzle posterior portion **17** of the pyrolysis chamber **11**. Vacuum seals (not shown) are advantageously employed at the points of entry of the connecting shaft **29** and the nozzled posterior portion **17** of the pyrolysis chamber **11** into the wall **19**. Said vacuum supporting wall **19** is preferably detachably connected to permit said wall **19** to be opened into two sections so as to permit entry and exit of coating chamber **23**. An aperture **27** in said wall **19** leads to a vacuum pump (not shown) or suitable vacuum unit.

Referring now to FIG. 2, the cross-sectional view **2—2** of the coating chamber **23** of FIGURE 1, shows in detail the baffles **21** provided within said coating chamber **23** whereby the tumbling motion of the particulate material disposed within said coating chamber **23** is enhanced.

While FIG. 2 shows a plurality of baffles, however, a greater or lesser number of baffles can satisfactorily be employed provided that the particulate material disposed within the coating chamber **23** is continuously agitated and said agitation is augmented by the said baffles **21**.

The quantity of material handled by the present apparatus is limited only by the size of the coating chamber **23**.

In order to insure uniformity of coating, the coating chamber **23** is advantageously rotated at from about 10–500 r.p.m. thus continuously tumbling the particles and exposing fresh surfaces to the condensing diradicals.

Premature condensation and polymerization of the diradicals on surfaces other than those presented in the coating chamber is prevented by maintaining all surfaces in contact with the diradicals except those within the coating chamber at temperatures above about 150° C.

Other obvious modifications can be made to this apparatus as desired. For example, means for continuously or batch-wise feeding of the di-p-xylylene to the vaporization section of tube **11** can be employed using vacuum traps or positive displacement feed units sealed to vacuum. Likewise, continuous feed of particulate material to be coated in chamber **23** can be provided without departing from the scope and intent of the present invention.

It is also within the concept of this invention to simultaneously deposit the poly(p-xylylene) and the metal, or to do so alternatively, i.e. by first depositing a coating of polymer or of metal and alternating layers of each on the particulate propellant component. This can be done merely by decreasing the temperature of the metal evaporation source **14** to a temperature insufficient to evaporate the metal but hot enough to prevent the polymer from forming on it during the first application of polymer coating in chamber **23** by pyrolysis of the di-p-xylylene in pyrolysis zone **11**. After the polymer coating is applied, heater **13** can be shut off and thus shut off the flow of vaporized di-p-xylylene to the pyrolysis chamber and the variac **18** adjusted to supply sufficient current to the metal evaporation source **14** to vaporize the metal for its coating on the particles in chamber **23**. However, there is seldom need to resort to alternative coating if the polymer coating is selected with care so as to be nonreactive with the propellant component.

In accordance with the preferred mode for carrying out the present invention, a measured quantity of the appropriate di-p-xylylene is placed within the vaporization zone of the pyrolysis chamber and a measured quantity of the selected metal placed in the metal evaporation source in the coating chamber. The system is evacuated to the selected pressure level necessary to vaporize the metal, and the di-p-xylylene is then vaporized and passed through the pyrolysis zone and through the nozzled portion of the pyrolysis chamber into the coating chamber which is under vacuum and maintained in a rotary motion. The diradicals contact the particulate propellant component while said material is being continuously tumbled within the coating chamber and condense on the surfaces of said material thus forming a complete coating of poly(p-xylylene) on the particles. After this, sufficient heat is applied to the metal evaporation source to vaporize the metal and thus coat the particles with the metal in the same manner, desirably together with the polymeric film of the poly-p-xylylene. After the desired thickness of coating has been maintained, the unit can be turned off and the coated particle recovered from the coating chamber.

The thickness of the coating is not narrowly critical but is dictated by the intended end use of the product. Certain materials may be coated with only a very thin coating of 0.1 mil or less where only resistance to solvent or reactive attack is desired. With other materials which may be subjected to mechanical abuse during subsequent handling and use, it may be desired to coat the particles quite heavily with one mil or more of polymer and metal particularly where it is desired to have a high content of the fuel metal surrounding a potent oxidizer.

The following examples are illustrative of this inventon. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE 1

One-half gram of nitronium perchlorate (NO_2ClO_4) pellets, ⅛ inch in diameter and variable lengths ranging from about 1/16 inch to ½ inch and averaging about 40 pellets per gram, were transferred from the original container to a small bottle serving as a coating vessel in a dry box of dehumidified air and the bottle containing the pellets was immediately transferred to a coating chamber in the system.

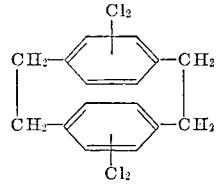
The coating chamber consisted of a two-piece glass chamber, overall dimensions of 3 inches in diameter and 12 inches long having a ground-glass joint at about the middle to allow the chamber to be opened. Through one end of the chamber is connected a glass inlet tube for feeding in the pyrolysis vapors of the substituted di-p-xylylene. The substituted di-p-xylylene is vaporized in glass chamber immediately preceding the pyrolysis zone. The vaporization chamber is maintained at a temperature of about 150–200° C. and connected to a quartz pyrolysis zone heated with an electric heating furnace to temtemperatures of 500°–700° C. for pyrolysis of the vapors.

Two outlets are provided in the coating chamber, one for attachment to the vacuum system, the other through a vacuum seal providing a stirrer bearing. A metal stirring shaft, ground to fit the stirrer bearing is inserted through the bearing and connected to motor means outside the coating chamber for rotating the stirrer at about 50–100 r.p.m. A bottle clamp or holder is attached to the end of the shaft inside the coating chamber for holding the bottle containing the pellets but providing for free tumbling of the pellets inside the bottle on the rotation of the shaft. The bottle clamp holds the bottle on its side during the coating and the inlet tube for feeding in the pyrolysis vapors enters into the mouth of the bottle holding the pellets to be coated when the unit is assembled.

A metal evaporation high heat pool located inside the bottle serves as the source of metal vapors for the coating, which is connected through insulated vacuum tight power leads to a power source, via an ammeter to the secondary leads of a current transformer. The primary leads are attached to a Variac transformer. The output of the current transformer was variable from zero to about 30 amperes. Aluminum metal is then placed in the melt pool before assembling.

After the unit is assembled and steady vacuum of 0.01 to 0.001 mm. Hg maintained, the motor was started and the bottle rotated at about 75 r.p.m. while feeding in dichloro-p-xylylene diradical vapors over a ten-minute period. The coating chamber was initially maintained at room temperature but the temperature gradually rose to about 40° C. at the end, due to feeding in the hot vaporous diradicals.

The dichloro-p-xylylene vapors were prepared by pyrolyzing tetrachloro-di-p-xylene having the formula



which was prepared as follows.

In a 500 ml., three-neck flask equipped with stirrer, addition funnel, and reflux condenser was placed 5.0 grams di-p-xylylene, 150 ml. of carbon tetrachloride and a pinch of iron powder. The flask was immersed in a water bath at 10° C. and a solution of 6.8 g. of chlorine in 150 ml. of carbon tetrachloride added to the stirred mixture over a period of one hour. The solution was stirred for an additional hour, heated to reflux to drive off the by-product hydrogen chloride, and filtered to remove the iron. The solvent was removed by atmospheric distillation and the product purified by vacuum distillation. A total of 7.1 g. of tetrachloro-di-p-xylylene (85% yield) B.P. 180–190° C. at 0.2 mm., M.P. 130–140° C. was obtained. The material contained 40.7 percent chlorine by elemental analysis compared with the theoretical value of 41 percent chlorine for tetrachloro-di-p-xylylene.

The dichloro-p-xylylene diradicals were prepared by pyrolysis of 2.0 grams of tetrachloro-di-p-xylylene, by vaporizing the tetrachloro-di-p-xylylene in the first heated chamber and passing the vapors through the pyrolysis chamber maintained at about 650° C. The residence time in the pyrolysis zone of the vaporized tetrachloro-di-p-xylylene was about .01 second which was sufficient to convert all of the tetrachloro-di-p-xylylene to the reactive dichloro-p-xylylene diradicals. The vaporous diradicals at a temperature of about 150° C. were fed directly into the coating chamber and onto the nitronium perchlorate pellets through the glass tube. The vaporous diradicals instantly condensed and polymerized on the surface of the nitronium perchlorate pellets and their rotation and tumbling in the bottle provided a coating of the poly(dichloro-p-xylylene) over the entire surface about 0.6 mil thick.

The thus coated pellets are then coated with aluminum by increasing the heat to the melt pool by adjusting the Variac so as to provide heat to the pool sufficient to melt the aluminum. Deposition of the aluminum can be observed by the formation of a mirror or dark cloudy formation on the walls of the coating chamber. Deposition is continued for several minutes to build up a sufficient layer of aluminum on the pellets.

It is preferred that this be done simultaneously with the polymer coating thereby locking in the vapor deposited aluminum to the coating. However, if desired, this can be done also by shutting off the current to the vaporization zone (and thus not pyrolyze the di-p-xylylene) and depositing only the aluminum.

After the desired amount of aluminum is deposited on the pellets, they can be given a final top coating of polymer which may or may not be the same polymer as the initial

coat. This is particularly desirable when it is desired to place a tougher, more impact resistant coating on the pellets as an additional safety feature, in the following manner.

The system was then brought back to atmospheric pressure and 3.0 grams of dichloro-di-p-xylylene was placed in the distillation and vaporization zone. The system was then re-evacuated to about 0.01 to 0.001 mm. Hg absolute and the coated pellets coated again with a top coating of poly(chloro-p-xylylene) in the same manner as above, in 10 minutes contact with the pyrolysis vapors of the dichloro-di-p-xylylene. The total thickness of the coating amounts to about 2 mils or more. The finished coated pellets could be exposed indefinitely to atmospheric conditions without effect.

Testing of the coating

In test tubes filled with 10 ml. water and 0.5 ml. of a universal pH indicator solution, there is added two of the nitronium perchlorate pellets coated as above with the poly(dichloro-p-xylylene) and aluminum. The initial pH of the solution was in the range of 5.5–6.0 as indicated by the color of the indicator solution in the tubes. After seventeen days, the solution of the tubes had a pH in the range of 3.5–4.5 indicating little if any hydrolysis of the nitronium perchlorate. As a control, when the pellets of several tubes were deliberately crushed, the pH immediately decreased to a pH of about 2 or less indicating a hydrogen ion concentration of 10^{-2}.

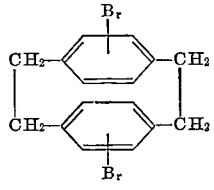
Complete immersion of the pellets having a top coat of the poly(chloro-p-xylylene) over the aluminum in a dilute hydrochloric acid solution show complete protection of the aluminum. The polymer is not affected by either the water or acid immersion.

EXAMPLE II

Employing exactly the same procedure as Example I, a first coating of poly(cyano-p-xylylene) was applied by the use of 2 grams of dicyano-di-p-xylylene placed in the distillation zone and the initial coating conducted over a ten minute period by condensing and polymerizing the cyano-p-xylylene diradicals on the surface of the nitronium perchlorate pellets. The first coating was evenly distributed over the entire surface of the pellet and was about 0.8 mils thick.

The dicyano-di-p-xylylene was prepared from the dibromo-di-p-xylylene as follows:

A mixture consisting of 5 grams of di-p-xylylene, 0.1 gram of iron powder and 400 ml. of carbon tetrachloride was placed in a 500 ml. 3 neck flask, equipped with a reflux condenser, stirrer and addition funnel. A solution of 10 grams of bromine in 50 ml. of carbon tetrachloride was added dropwise from this addition funnel to the stirred suspension over a 30 minute period. The reaction mixture was stirred at 10° C. to 20° C. for twelve hours. The catalyst was filtered off and the solution concentrated to 30 ml. by distillation. Upon cooling, di-bromo-di-p-xylylene crystallized from solution. The material was separated by filtration, and purified by sublimation. A total of 3.3 grams equivalent to 37 percent yield was obtained. The material had a melting point of 240° C.–242° C. The material analyzed for 43.5 percent bromine, as compared with the theoretical value of 43.7 percent for dibromo-di-p-xylylene, having the structure



Into a dry 100 ml. three-necked flask fitted with a reflux condenser protected from moisture with a drying tube, a thermometer, and a dry nitrogen-gas inlet was placed 7.32 g. of dibromo di-p-xylylene, 4.5 g. of dry cuprous cyanide and 20 ml. of dry quinoline. The mixture was heated at 210° C. to 230° C. for 20 hours with continuous stirring. After the reaction period the mixture was cooled to about 100° C. and poured into a mixture of 100 ml. each of benzene and a 29 percent aqueous solution of ammonium hydroxide. The concentration was half that of the commercially available aqueous ammonium hydroxide (58 percent). The mixture was shaken well until all the coarse particles disintegrated. The benzene layer was separated, washed with dilute aqueous ammonium hydroxide, water, and then filtered. After concentrating the benzene solution to dryness, the crude solid residue was distilled under vacuum to give a slightly colored crystalline product. The color is due to races of quinoline.

The distilled product was recrystallized from 95 percent ethanol to give an analytically pure product having a melting point of 165° C. to 167° C. and in a yield of 81 percent. Elemental analysis confirmed the structure.

Calcd. for $C_{18}N_{14}N_2$ (percent): C, 83.72; H, 5.43; N, 10.85. Found (percent): C, 83.45; H, 5.70; N,. 10.5. No bromine was detected.

Codeposition of aluminum and poly(cyano-p-xylylene) accomplished in the same manner as recited in example gives a suitably protected pellet of nitronium perchlorate.

EXAMPLE III

Employing the procedure described in Example I, five grams of dichloro-di-p-xylylene prepared in the same manner, was placed in the sublimation zone, and a small piece of aluminum was placed inside the tungsten wire basket inside the condensation chamber. The sublimation zone consisted of a 1½ inch x 10 inch sublimation zone surrounded by a heater capable of heating the zone to 125°–150° C. This zone was connected to a 1½ inch x 18 inch Vycor glass pyrolysis tube containing a 1½ inch x 15 inch Vycor glass insert. The pyrolysis tube was attached to a 3 inch x 15 inch glass deposition chamber having a rotatable unit for tumbling the particles. Vacuum lines connected the condensation chamber via a Dry-Ice trap, to an oil diffusion pump. The diffusion pump was backed by a mechanical pump. The copper wires were sealed into the deposition chamber. Inside the chamber a tungsten wire basket was placed across the copper wires and the aluminum placed in the tungsten basket. Outside of the deposition chamber the copper wires were attached via an ammeter to the secondary leads of a small (150 volt-ampere) current transformer. The primary leads were attached to a Variac transformer. Previous trails had shown that by vaying the voltage on the Variac, the output of the current transformer could be varied from zero to about 30 amperes.

Ammonium perchlorate pellets of a size passing about a standard No. 10 mesh screen were placed in the coating chamber so they would tumble when the chamber was rotated for receiving the coating.

After being assembled the equipment was evacuated to about 0.001 torr (0.001 mm. Hg). The pyrolysis tube was heated by an external furnace to 650° C. A current was supplied to the tungsten filament and a small portion of the aluminum evaporated as detected by it forming a miror on the glass walls of the deposition chamber. The current was decreased but not turned off. Then the furnace heating the sublimer tube was turned on and the temperature raised to 125° C. The dimer slowly sublimed from the sublimer tube into the pyrolysis tube (where it was thermally cracked to form chloro-para-xylylene) and thence into the deposition chamber where it deposited to form poly(chloro-para-xylylene). When deposition of polymer commenced in the deposition chamber (as evidenced by the rainbow-like interference pattern always seen in these polymerizations) the current to the tungsten filament was increased so that the remainder of the aluminum evaporated fairly rapidly. Where the aluminum was deposited slowly with the polymer a dark coating on the pellets and chamber walls forms. Here the aluminum is believed to be dispersed in the plastic as a smoke of

atomically dispersed aluminum. Most of the aluminum was deposited rapidly and in these areas a bright coating was formed. After all the aluminum had evaporated the temperature on the sublimer furnace was increased to 180° C. and the last portion of the polymer was deposited rapidly. The heaters were then shut off.

The unit was permitted to cool down before the vacuum was broken. The ammonium perchlorate pellets coated simultaneously with poly(chloro-p-xylylene) and aluminum is completely impervious to moisture, as determined by complete immersion in water as in Example I. The final top coating polymer after the aluminum coating on the pellets completely protects the aluminum from attack, as determined in a similar test using dilute hydrochloric acid as the test reagent.

This same procedure can be used for coating of any other potent propellant component as hereinbefore described.

EXAMPLE III–A

Using the same equipment and the same general procedure as described in Example II, aluminum and poly(chloro-p-xylylene) was alternatively deposited. Again 5.0 grams of dichloro-di-p-xylylene was used. After the equipment was assembled, it was evacuated to less than 0.001 torr. A small portion of the aluminum was evaporated as indicated by a mirror surface on the glass chamber walls. Then the temperature of the sublimer tube was raised to 175° C., a portion of the dimer was sublimed and a layer of polymer was deposited. At this point the sublimation of dimer was temporarily stopped and the remainder of the aluminum was evaporated. Finally, the last of the dimer was sublimed and a second layer of polymer deposited. After the polymer deposition is completed the unit was shut down to cool and vacuum broken.

There was thus formed in this experiment a laminar polymer-aluminum-polymer coating. Ammonium perchlorate pellets coated by this technique have a shiny surface, completely protected with two coats of polymer sandwiching a coating of aluminum. Any thickness of metal coating can be built up between the polymer coatings so as to provide the desired amount of metal-to-polymer coating. Pellets coated in the above manner show only a very slow reaction on immersion in dilute hydrochloric acid whereas other pellets not having the final top coating of polymer react very quickly, thus dissolving out the metal.

Thus this example illustrates that the metal fuel itself can be effectively protected by this invention.

EXAMPLE IV

Employing the same technique and equipment as described in Example III, lithium metal was codeposited with poly(dichloro-p-xylylene).

Tetrachloro-di-para-xylylene, 10.0 g., was placed in the sublimation tube. A piece of lithium wire, about ⅛ inch diameter and about ⅜ inch long, was placed in the tungsten wire coil basket. Lithium aluminum hydride pellets in the coating chamber were checked to see if they satisfactorily tumbled on rotating of the chamber. After being assembled, the equipment was evacuated to about 0.001 torr. A small, 4-ampere, current was caused to flow through the evaporator circuit, warming it and thus preventing unwanted deposition of polymer on this portion of the apparatus. Sublimation of the dimer was begun by increasing the temperature in the sublimer furnace to about 180° C. Deposition of poly(dichloro-para-xylylene) began soon after this temperature was reached. After deposition of polymer had begun the current on the evaporator circuit was increased to about 8 amperes. The lithium wire contained in the tungsten wire basket melted and evaporated smoothly over a period of about five minutes. After the lithium evaporation was complete the remainder of the dimer was evaporated and the apparatus cooled and opened to the atmosphere.

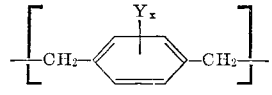
Lithium aluminum hydride pellets so coated are protected by a smooth tough adherent coating of poly(dichloro-p-xylylene) and lithium metal completely around the pellets. Pinholes in such coated pellets are rare and can be completely eliminated by longer coating times permitting a heavier polymer coating.

The film coating on the pellets is generally black and opaque when a heavy coating of lithium is present but is clear and brown in color when lower amounts of lithium are used. The polymer coating containing a high concentration of lithium burns quite vigorously on ignition.

Sodium, boron and beryllium are deposited by the same technique as above described, either by the alternative coating or by the codeposition technique of the examples. However, with the hazardous metals, it is preferable that the last coating on the propellant component be of the poly(p-xylylene).

What is claimed is:

1. A coated particulate solid propellant component having as an encapsulating coating thereon, a continuous coating comprising a light metal having an atomic weight below 27 in vapor deposited form and a tough, solvent resistant linear polymer having the general repeating unit



wherein Y is an inert aromatic nuclear substituent group having a sigma para value from about zero to about +0.8 and commensurate with the reactivity of the said particulate component, and x is an integer from 1 to 3 inclusive.

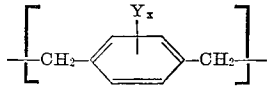
2. A coated particulate solid propellant component defined in claim **1** wherein the component is a potent oxidizer.

3. A coated particulate solid propellant component defined in claim **1** wherein the component is a potent reducing agent.

4. A coated particulate solid propellant component defined in claim **1** wherein the light metal is alternatively deposited in laminar form on the particle.

5. A coated particulate solid propellant component defined in claim **1** wherein the light metal is codeposited with polymer on the particle.

6. A unitary propellant formulation comprising a particulate solid potent oxidizer having a tough adherent coating thereon encapsulating the oxidizer comprising a light metal having an atomic weight below 27 in vapor deposited form and a tough solvent-resistant linear polymer having the general repeating unit



wherein Y is an inert aromatic nuclear substituent group having a sigma para value from about zero to about +0.8 and commensurate with the reactivity of the oxidizer, and x is an interger from 1 to 3 inclusive.

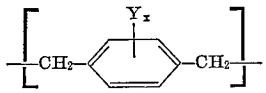
7. A unitary propellant formulation described in claim **6** wherein the oxidizer is nitronium perchlorate and the sum of the sigma para value of the substituent groups is at least 0.4.

8. A unitary propellant formulation described in claim **6** wherein the oxidizer is ammonium perchlorate.

9. A unitary propellant formulation described in claim **6** wherein the oxidizer is lithium perchlorate.

10. Solid particulate having nitronium perchlorate having a tough continuous impervious coating encapsulating the particles, said coating comprising a light metal having an atomic weight below 27 in vapor de-

posited form and a linear polymer having the general repeating unit



wherein Y is an inert aromatic nuclear substituent group having a sigma para value from about +0.2 to +0.8, and x is an integer from 1 to 3, inclusive, with the sum of the sigma para values of the Y substituent groups being at least about +0.4.

11. Solid particulate nitronium perchlorate described in claim **10** wherein the Y group is at least one cyano group.

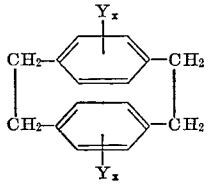
12. Solid particulate nitronium perchlorate described in claim **10** wherein the Y group is chlorine and x is an integer of at least 2.

13. Solid particulate nitronium perchlorate described in claim **12** wherein the light metal is aluminum.

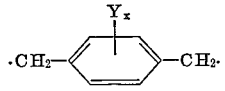
14. Solid particulate nitronium perchlorate described in claim **13** wherein the aluminum is alternatively deposited in laminar form on the particle.

15. Solid particulate nitronium perchlorate described in claim **13** wherein the aluminum is codeposited with polymer on the particle.

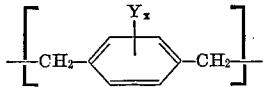
16. A method for coating of solid particulate propellant components which comprises the steps of pyrolyzing at a temperature between about 450° C. and 700° C. a cyclic di-p-xylylene having the general structure



wherein Y is an inert aromatic nuclear substituent group having a sigma para value from about zero to about +0.8 and commensurate with the reactivity of the component to be coated, and x is an integer from 1 to 3, inclusive, thus forming reactive diradicals having the general structure



wherein x and Y are as defined above, depositing the thus formed diradicals on the surface of solid particulate propellant components while maintaianing the particles in constant motion to continually expose fresh surfaces to said diradicals and depositing vapors of a light metal having an atomic weight below about 27 onto the surface of the moving particles, said particles being maintained at a temperature below 200° C. and below the condensation temperature of the reactive diradicals and the metal vapors, whereby the reactive diradicals and the said metals condense on the surface of the particles thereby coating said particles with a continuous coating of the said metal and a polymeric film of poly(p-xylylene) having the general repeating unit



wherein Y and x are as defined above.

17. A method as defined in claim **16** wherein the light metal is alternatively deposited in laminar form on the particle.

18. A method as defined in claim **16** wherein the light metal is codeposited with polymer on the particle.

References Cited

UNITED STATES PATENTS

3,190,776	6/1965	Enden	149—8
3,402,065	9/1968	McDonald	149—7 XR
3,070,469	12/1962	Jenkin	146—5
3,035,948	5/1962	Fox	149—19
3,006,743	10/1961	Fox	149—19
3,002,830	10/1961	Barr	149—19

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