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**LEAD AZIDE-ELASTOMER EXPLOSIVES IN
FILM AND SHEET FORM**

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United States of America as represented by the Secretary of the Army
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This invention relates to explosives and more particularly concerns improved methods for making lead azide explosives in film and sheet form.

The detonation velocity of crystalline lead azide is approximately $\frac{1}{2}$ that of pentaerythritol tetranitrate (PETN) (4070-5180 vs. 8300 meters per second). Lead azide does not produce large amounts of gas as does PETN when subjected to elevated temperatures. Further, a lead azide film composition will propagate reliably using only small quantities of actual explosive spread over a given area (about 0.25 g./4 sq. in. of lead azide vs. about 0.976 g./4 sq. in. for PETN sheet explosive). This ability to readily propagate permits the use of a thickness of lead azide of only approximately 0.003 inch as opposed to a thickness of about 0.014 inch for a PETN sheet.

Lead azide is light-sensitive. When made into convenient sheet form, it may be ignited by exposing it to a high intensity light such as that produced by an argon bomb or laser. A backing sheet of secondary explosive could, in turn, be detonated. The argon bomb light could also be used to detonate the lead azide sheet and thereby cause it to act as a plane wave generator. Similarly, a lead azide sheet explosive could be used more safely and conveniently in applications such as military initiators, for example, where loose powder is generally currently used therein.

Heretofore, the preparation of lead azide sheets was considered hazardous. The process employed for the preparation thereof necessitated a final "rolling-out" to the desired thickness which, in the past, has oftentimes resulted in explosions. Other methods for preparing thin lead azide sheets were also accompanied with varying degrees of danger.

It is therefore an object of this invention to provide elastic thin films of explosive material.

Another object of the invention is to provide thin films of lead azide for use in low impulse explosives.

Still another object of the invention is to provide methods for the preparation of thin films of lead azides for use in low impulse explosives, said methods being characterized by a high degree of safety, economy and reproducibility.

Other objects and advantages of the invention will be apparent as the description of the invention proceeds.

Briefly, I have discovered that colloidal lead azide, when precoated with polyvinyl pyrrolidone (PVP), may be dispersed in a suitable elastomer latex to form a thin film of lead azide having the properties and characteristics aforementioned.

More specifically, my thin films of insensitive lead azide may be prepared by first coating colloidal lead azide with PVP having a molecular weight of about 90,000. This precoating of the lead azide with a very thin film of an adhesive polymer is advantageous in providing a margin of safety in handling the recognized hazardous initiator explosive, colloidal lead azide.

My procedure for precoating (0.1% PVP) is as follows:

(1) Make a solution by stirring PVP powder (.0328

2

gram (into cold water to dissolve. Add hot water to make 10 ml.

(2) Pour the warm solution into a beaker containing 32.8 grams of pure colloidal lead azide. Mix to form a uniform dampened mass, using a wooden spatula.

(3) Spread the mass out on a tray to air dry at ambient temperature, overnight.

(4) Transfer the dried precoated frangible powder into a conductive rubber beaker to store.

Alternate procedure: same as above except that PVP may be dissolved in a mixture of 5 ml. distilled water and 5 ml. of ethanol for faster drying.

Having precoated the lead azide, processes for forming thin sheets thereof will be described using the illustrative examples below. The sheet explosives comprised a high filler loading (about 79-91%) of finely divided net lead azide content (about 1 to 5 microns in diameter) in a suitable film-forming binder. Hazards are substantially eliminated by using binders containing water instead of flammable solvents and in processing the material to desired thicknesses without rolling.

Example I (about 85% net lead azide content)

Add 0.02 gram of a thickener such as guar gum powder to 0.422 gram of an elastomer latex such as Kel F-5500, a trademark product of Minnesota Mining and Manufacturing Company, comprising a fully saturated copolymer of chlorotrifluoroethylene and vinylidene fluoride containing more than 50% of fluorine by weight, heavy white water dispersion of 60% total solids having a particle size ranging between 0.2 to 0.3 micron, viscosity, 77° F., cps. of 57 and a 1.84 specific gravity of solids and 1.45 specific gravity of liquid, water latex. The guar additive serves as a suspending agent as well as to prevent the discontinuity and lifting of the final film.

Stir in 0.6 gram water to the above mixture to form a slurry. Now add 1.25 grams of the precoated lead azide to the slurry until a gel paste dispersion results. This paste is now ready to be spread onto an inert substrate such that one gram of lead azide will cover a 4" x 4" area. The substrate may be a taut, levelled polyethylene sheet, for example, which was previously wiped with an adhering agent such as about a 25-40% acrylonitrile type butadiene-acrylonitrile water dispersion of about 5 to 25% solid particles of about 500 Angstroms diameter to promote adhesion of the lead azide film to the polyethylene. The addition of more water may be required to spread the gel conveniently and uniformly. The coated polyethylene sheet, 4" x 4" is then allowed to dry at room temperature. Within one hour or less, however, loss of a small amount of water by evaporation results in the inversion of the filled latex to a continuous film.

The explosive film for convenience and added strength and flexibility may remain bonded to a very thin substrate, for example the polyethylene sheet aforementioned, or the film may be coated directly onto any desired surface by brush-coating the gel-water dispersion of explosive onto the substrate.

The 4" x 4" sheet had a thickness of from .0025 to .004 inch (one gram on 16 square inches) and yielded only $\frac{1}{8}$ the specific impulse of the thinnest practicable PETN-based sheet explosive (.014 inch thickness—1 gram PETN covered 4 square inches approximately). My sheet detonated and propagated completely.

Water dispersible elastomers other than Kel-5500 may be used advantageously. For example, butadiene has been found to work admirably. Similarly, a copolymer of styrene-butadiene, wherein the butadiene is present in an

3

amount of at least about 60%, and polyisobutylene are satisfactory.

To prevent the surface of the lead azide-based film from ultraviolet discoloration (browning) by sunlight or when exposed to outdoor light rays, the spreading of about 5% by weight (based on the weight of the original ingredients) of a yellow dye such as di-1,5-chloroanthraquinone to the film, while yet tacky, has been found most effective.

Example II

Mix about 84 grams of colloidal lead azide precoat with 0.1% PVP having a molecular weight of about 90,000 into about 29 grams of butyl latex having about 55% solids content, the solid particles of butyl rubber being about 0.05 to 1.0 micron in diameter, to form a slurry. On a leveled sheet of about 0.060" thick polyethylene sheet of sufficient area, thinly wipe on an adhering agent such as di-n-hexyl azelate. Meter out 1.8 grams of the above slurry onto a 2" x 2" portion of the polyethylene which had previously been marked off thereon. Tamp the assembly to spread out the thixotropic latex dispersion evenly in this area. Optionally, one may brush-coat or dip-coat the thixotropic latex dispersion of explosive onto any desired substrate surface such as a sphere. Allow to dry at ambient temperature. Within about one hour, the loss of a small amount of water by evaporation will result in the inversion of the system and the setting of the filled latex to a continuous film. Continue drying overnight at ambient temperature until a constant weight of the lead azide-based film is obtained.

The dried film will contain about 84% lead azide. The butyl latex content of the dried film may vary from about 10 to 21% whereas the lead azide may vary from about 79 to 90%. Some specific values of various physical properties of the above film will be tabulated hereinafter.

Example III

Impregnate a lightweight flexible polyurethane foam of about $\frac{1}{64}$ inch thickness (5 to 10 pounds per cubic foot) having a uniform structure of honeycomb pores with the gel paste dispersion described under Example I.

The impregnated foam may constitute between about 4 to 8 weight percent of the final flexible discrete explosive sheet.

Example IV

Prepare two .058" thick polyethylene sheets by spraying them with any suitable mold releasant, such as silicone mold lubricant or fluorocarbon dry lubricant. Optionally, two smooth, flat slabs of silicone rubber may be used. Mark off on one of the sized sheets a $3\frac{1}{2}$ x 1 inch rectangular area using polyethylene-backed adhesive tape strips for the boundaries. Mix 0.2 grams of a liquid polyurethane prepolymer, such, for example, as the reaction product of 2,4-tolylene diisocyanate and 1,4-butylene oxide polyglycol, with an equal amount of a plasticizer, di-n-hexyl azelate. Stir in 1.5 grams of colloidal lead azide, precoat with 0.1% by weight PVP having a molecular weight of about 90,000. Doctor blade this paste composition over the rectangular area marked as above. The effective composition weight applied was 1.46 grams, consisting of 1.15 grams of pure colloidal lead azide. Place the second polyethylene sheet on top to form a sandwich type construction. Place weights on top to spread out the composition over the bonded area. A uniform spread is now readily attainable. Heat the assembly containing the polyethylene-confined lead azide composition on a steam plate at about 80° C. overnight.

If desired, remove the discrete film explosive by carefully lifting the polyethylene backings, using a spatula as needed. The resulting film, 0.013" thick, contains 79/21 lead azide/plasticized polyurethane elastomer. The net lead azide content of the final film may be effectively varied between about 79 to 90% by weight.

4

Specific values of various physical properties of the above lead azide film are tabulated below:

TABLE I.—CHARACTERISTICS OF LEAD AZIDE SHEET EXPLOSIVES: SENSITIVITY AND STABILITY

	Example II	Example IV
Lead azide content, percent, approx.....	84.0	79.0
Type binder.....	(1)	(2)
120° C. vacuum stability test* (see text), 2.3 gm., 40 hrs., ml. of gas.....	0.31	1.22
Impact sensitivity* (see text):		
Picatinny Arsenal apparatus, 2 kg. wt.; in.....	6	6
Charge wt., grams.....	.030	.062
Bureau of Mines apparatus, 2 kg. wt., cm.....	9	5
(Charge in the form of cut discs)		
15 Electrostatic sensitivity test** (see text) (using cut discs):		
Minimum ignition level (1 ignition in 10 trials), joules.....	0.026	11.025+
Volts.....	5,100	5,000
C, microfarads.....	.002	.882
Resistance, ohms.....	0	0
Relative humidity, percent.....	31	51
Temperature, ° C.....	25.3	28
Flame test.....	(3)	(4)
Means of initiating detonation.....	Mild detonating fuze .014- inch-thick, 75% PETN with elastomeric binder	

- 25 1 Modified butyl.
2 Plasticized polyurethane.
3 Detonates.
4 Burns, snaps.

*120° C. Vacuum Stability Test and Impact Sensitivity Test (Picatinny Arsenal and Bureau of Mines) are described in "Standard Laboratory Procedures for Sensitivity, Brisance and Stability of Explosives," Arthur J. Clear, Feltman Research Laboratories, Picatinny Arsenal, Dover, New Jersey, January 1961, pages 31 to 37 and pages 1 to 13 respectively.

**Electrostatic Sensitivity Test is described in "Sensitivity of Explosives to Initiation by Electrostatic Discharges," S. W. Brown, D. J. Kusler, S. C. Gibson, Bureau of Mines Report of Investigation, No. 5002, Pittsburgh, Pennsylvania, September, 1953. This report gives the highest energy in joules for zero probability ignition. For example, pure colloidal lead azide is reported as .001 joule; PETN through 100 mesh, 0.062 joule; nitrocellulose (13.4% N), .062 joule.

By the procedures described above, other explosives may be prepared similarly in generally thin sheets of films. Thus, explosives such as lead styphnate, mannitol hexanitrate, PETN and mixtures thereof, for example, may be substituted for the lead azide specifically hereinabove exemplified.

I claim:

1. A process for the preparation of explosive lead azide thin films which detonate and propagate completely, said film having a specific impulse of as low as about $\frac{1}{8}$ that of a comparable pentaerythritol tetranitrate thin explosive film and comprising the steps of
precoating colloidal lead azide with 0.1% by weight polyvinyl pyrrolidone having a molecular weight of about 90,000,
adding guar gum powder thickener to a water-dispersed elastomer to form a mixture,
stirring water into said mixture to form a slurry,
adding said precoated lead azide into said slurry to form a gel paste dispersion,
thinly and uniformly spreading said gel paste dispersion onto an inert substrate, and
drying said dispersion on said substrate to form a dried thin film of explosive lead azide.

2. A process as described in claim 1 wherein said gel paste dispersion is impregnated into a lightweight honeycomb flexible foam plastic to form a flexible discrete explosive sheet.

3. The process as described in claim 1 wherein said dried thin film of explosive lead azide comprises about 79 to 90% by weight lead azide, about 1 to 2% by weight guar gum, and about 8 to 29% weight elastomer.

5

4. The process as described in claim 1 wherein said elastomer is a material selected from the group consisting of butadiene, a copolymer of styrene-butadiene wherein said butadiene is present in an amount of at least about 60%, polyisobutylene, and a fully saturated copolymer of chlorotrifluoroethylene and vinylidene fluoride, said fully saturated copolymer comprising a water dispersion of about 60% solids having a particle size ranging between about 0.2 to 0.3 micron, and a specific gravity of about 1.84, said fully saturated copolymer containing more than 50% fluorine by weight.

5. The process as described in claim 3 wherein said dried thin film has a thickness of between about 0.0025 inch and 0.004 inch.

6. The process as described in claim 3 wherein said dried thin film has its surface coated with di-1,5-chloro-anthraquinone to prevent ultraviolet discoloration of said film.

7. A process for the preparation of explosive lead azide thin films, said thin films exhibiting excellent thermal stability, low impact sensitivity and low sensitivity to sparks and comprising the steps of

precoating colloidal lead azide with about 0.1% by weight polyvinyl pyrrolidone having a molecular weight of about 90,000,

adding said precoated lead azide into butyl water latex to form a slurry, said butyl latex comprising about 55% solids of about 0.05 to 1.0 micron diameter, uniformly and thinly spreading said slurry onto an inert substrate, and

drying said slurry on said substrate to form a dried thin film of explosive lead azide.

8. The process as described in claim 7 wherein said dried thin film of explosive lead azide comprises about 79 to 90% by weight lead azide and the balance being substantially butyl elastomer.

9. A process for the preparation of explosive lead azide thin films, said thin films exhibiting excellent thermal stability, extremely low sensitivity to shock and comprising the steps of

precoating colloidal lead azide with about 0.1% by weight polyvinyl pyrrolidone having a molecular weight of about 90,000,

6

adding about equal amounts of di-n-hexyl azelate plasticizer and polyurethane prepolymer comprising the reaction product of 2,4-tolylene diisocyanate and 1,4-butylene oxide polyglycol to form mixture, stirring said precoated lead azide into said mixture to form a paste,

spreading said paste onto one sheet on an inert substrate,

sandwiching said pasted substrate by placing another sheet of similar inert substrate atop thereof,

drying said sandwiched paste to form a resultant film, and

removing said resultant film from said substrate.

10. The process as described in claim 9 wherein said resultant film is about 0.013 inch thick.

11. The process as described in claim 9 wherein said resultant film comprises about 79 to 90% by weight lead azide and the balance being substantially plasticized polyurethane elastomer.

12. A process for the preparation of low impulse explosive lead azide thin films, comprising the steps of precoating colloidal lead azide with a thin coating of high molecular weight polyvinyl pyrrolidone,

uniformly mixing said precoated lead azide with a semi-solid polymeric carrier therefor,

uniformly spreading said mixture onto an inert substrate, and

drying said mixture on said substrate to form a dried thin film of low impulse explosive lead azide.

13. The process according to claim 12 wherein said semi-solid polymeric carrier is selected from the group consisting of a thickened water dispersion of an elastomer, butyl water latex and a plasticized polyurethane prepolymer.

14. A low impulse explosive lead azide thin film made by the process of claim 12.

No references cited.

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