

[54] **COMBUSTIBLE CARTRIDGE CASE**

[75] Inventors: **Sydney Axelrod**, New York, N.Y.;
Walter Brenner, Teaneck, N.J.

[73] Assignee: **The United States of America as represented by the Secretary of the Army**, Washington, D.C.

[22] Filed: **Apr. 23, 1974**

[21] Appl. No.: **463,237**

[52] U.S. Cl. **102/43 R; 102/38; 102/DIG. 1**

[51] Int. Cl.² **F42B 9/16; F42B 5/18**

[58] Field of Search **102/43 R, 43 P, 38, DIG. 1**

[56] **References Cited**

UNITED STATES PATENTS

3,264,993	8/1966	De Fries et al.	102/DIG.1
3,504,630	4/1970	Picard	102/43 R

3,550,532	12/1970	Zimmerman	102/43 R
3,670,649	6/1972	Hartlein et al.	102/DIG. 1
3,703,868	11/1972	Braak	102/DIG. 1
3,730,094	5/1973	Quinlan	102/43 P

Primary Examiner—Charles T. Jordan

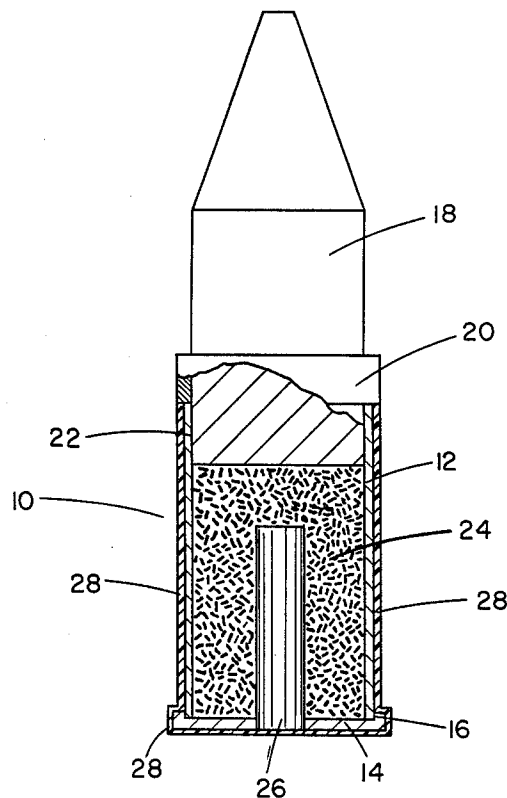
Attorney, Agent, or Firm—Nathan Edelberg; Robert P. Gibson; A. Victor Erkkila

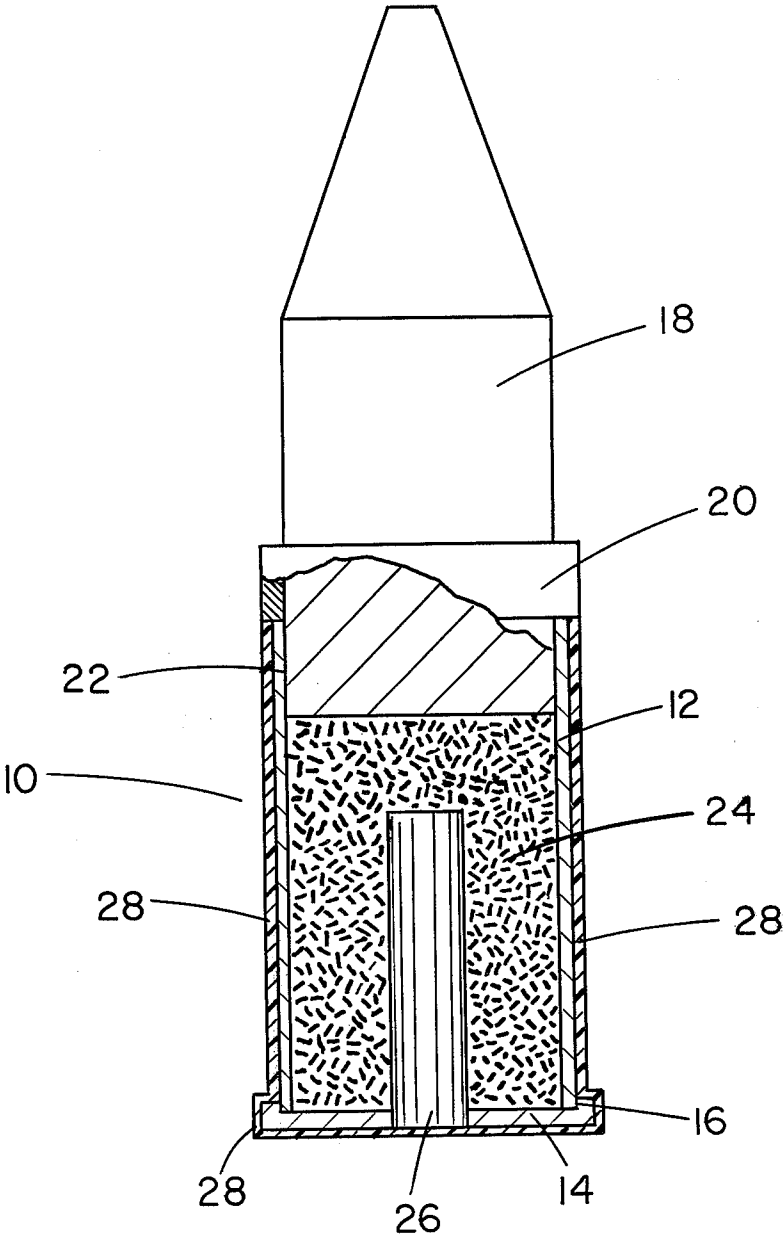
[57]

ABSTRACT

Porous combustible cartridge cases containing nitro-cellulose, reinforcing fibers and a resinous binder, are rendered resistant to water and oil by providing the exterior surface with a consumable coating consisting essentially of RDX, HMX or PETN dispersed in a polymeric resin, e.g., an alkyl methacrylate, which is capable of thermally depolymerizing to the monomer.

5 Claims, 1 Drawing Figure





COMBUSTIBLE CARTRIDGE CASE

BACKGROUND OF THE INVENTION

This invention relates to a novel and improved combustible, non-metallic cartridge case, and particularly to a porous, fiber reinforced nitrocellulose cartridge case provided with a coating, which is resistant to penetration by water and oil and promotes the complete consumability of the cartridge case.

Combustible cartridge cases are generally composed of nitrocellulose, reinforcing fibers and a resinous binder. A case of such type is filled with a propellant and fitted with a primer and a projectile to form a cartridge. Compared with metallic cases, the non-metallic cartridge cases possess the dual advantages of lower weight and cost.

A common method of fabricating combustible, non-metallic cartridge cases comprises dispersing nitrocellulose fibers or powder, reinforcing fibers, such as kraft and other cellulosic fibers, and synthetic fibers, such as acrylics and polyesters, together with resin binders and other components, i.e., stabilizers, etc., in water and collecting the fibers on a felting die. The felted fiber form is then molded into the desired shape using appropriately shaped matched molds, cured and dried. The finished cartridge case has a porous fibrous structure, which must be maintained to ensure the rapid propagation of the flame through the case material during firing. However, due to its porous structure and content of fibers, particularly cellulosic fibers, the non-metallic cartridge case will absorb liquid water as well as permit the penetration of water vapor, which adversely affects the firing and ballistic performance of the ammunition and causes incomplete combustion of the cartridge case. In addition, contact with oily substances, such as hydraulic fluids, also degrades the combustion characteristics of such non-metallic cartridge cases.

Various attempts to overcome the aforesaid deficiencies have included coating the cartridge case surface with a plastic film, such as nitrocellulose, alkyd resins, and polyvinylbutyral resins. Generally, it was found that if a coating was thick enough to protect the cartridge case against both liquid water and water vapor, the flame could not propagate throughout the case during the firing cycle with the result that the case did not burn completely and left residue in the gun. On the other hand when the amount of coating was reduced so that the coating did not interfere with the combustion of the case, the coating failed to adequately protect the case against the penetration of liquid water and water vapor, which also produced an incomplete combustion of the case with resultant residue in the gun. Such residue presents an intolerable hazard, since it can smolder and cause accidental preignition of the cartridge case of the next round loaded into the gun. In addition, absorbed water or water vapor degrades the ballistic performance of the ammunition.

An object of the present invention is to provide a coating, which will render the combustible cartridge case insensitive to water and oil.

Another object of the invention is to provide a combustible cartridge case whose exterior surface is coated with a composition, which renders the case substantially impermeable to water and oil, so that upon firing of the ammunition the ballistic level of the ammunition will not be adversely affected and little, if any, residue

will remain in the gun due to the coating or the absorption of water or oil by said case.

The foregoing and other objects will become apparent from the following disclosure.

SUMMARY AND DETAILED DESCRIPTION OF THE DRAWING AND THE INVENTION

The drawing illustrates a longitudinal cross-sectional view of a typical, assembled combustible cartridge. As shown in the drawing, the assembled cartridge comprises a generally cylindrical cartridge case 10 consisting of a tubular casing 12 and a base element 14, which can be attached to the lower end of casing 12 by adhesive means 16. A metal projectile 18 provided with a rotating band 20 is mechanically or adhesively attached to the upper end 22 of casing 12. A suitable propellant 24, e.g. nitrocellulose grains, is contained in the case 10 and is ignited by a primer 26 mounted in the base element 14.

In accordance with the present invention the exterior surface, at least, of the combustible cartridge case 10 is completely coated with a novel coating composition 28 more fully described hereinafter. Further, the cartridge case 10, which is coated according to the present invention, is a well-known type of porous combustible cartridge case, which is composed of a nitrocellulose of moderate nitrogen content, reinforcing fibers, e.g. Kraft or synthetic fibers such as acrylics, and a resinous binder, such as polyvinylacetate, and is formed by conventional methods, e.g. felting or compression molding.

In accordance with this invention, there is provided an improvement in porous combustible cartridge cases containing nitrocellulose, reinforcing fibers and resin binders, wherein at least the exterior surface of the case is covered with a novel coating consisting essentially of a dispersion of finely divided particles of RDX (cyclotrimethylenetrinitramine), HMX (cyclotetramethylenetetranitramine) or PETN (pentaerythritol tetranitrate) in a polymeric resin, which is capable of thermally depolymerizing to the monomer, selected from the group consisting of alkyl methacrylate polymers, methacrylonitrile polymers, and alpha methyl styrene polymers. Such coating prevents the penetration of oil and water, including liquid water and water vapor, into the porous surface and interior of the cartridge case. Under the elevated temperatures produced when the round is fired, the resin depolymerizes to the volatile monomer and the solid high energy explosive, e.g., RDX, assists in burning the resin as well as the case, whereby little or no residue is left in the gun.

The novel coating compositions can be prepared by dispersing or dissolving the high energy explosive, such as RDX, in a solution of a solid resin of the aforesaid class in a suitable liquid organic solvent. Suitable organic solvents do not affect the case deleteriously and include benzene, toluene, hexane and mixtures thereof, methylene chloride and perchloroethylene. The liquid coating compositions can be applied to the cartridge case by usual methods such as spraying, brushing and dipping, the viscosity of the solution depending on the method of application.

The proportions of high energy explosive, polymeric resin and solvent in the coating solution may vary widely depending on the specific service requirements. In general, the solids or non-volatile portion of the liquid coating composition contains between 30 and 90 weight percent of the high energy explosive and between 70 and 10 weight percent of the polymeric resin.

Also, the solids content of the coating solution can range from about 5 to 50 weight percent, depending on the method of application to the combustible cartridge case. A preferred formulation for such compositions comprises about 80 weight percent of RDX or other high energy explosive, and about 20 weight percent of alkyl methacrylate polymer, or other polymer of the aforesaid group, dissolved in a liquid solvent, especially wherein the high energy explosive and polymeric resin solids constitute about 25-35 weight percent of the solution.

The following illustrates representative liquid coating compositions of the present invention:

a.	methylene chloride	220 grams
	ethyl methacrylate polymer	20 grams
	butyl methacrylate polymer	5 grams
	RDX	80 grams
b.	methylene chloride	110 grams
	toluene	110 grams
	ethyl methacrylate polymer	20 grams
	butyl methacrylate polymer	5 grams
	PETN	80 grams
c.	methylene chloride	50 grams
	toluene	160 grams
	ethyl methacrylate polymer	25 grams
	methyl methacrylate polymer	5 grams
	HMX	90 grams
d.	methylene chloride	48 grams
	toluene	96 grams
	hexane	96 grams
	methyl methacrylate polymer	18 grams
	butyl methacrylate polymer	2 grams
	RDX	83 grams

The amount of resin-explosive composition coated on the cartridge case surface can be varied widely. Generally, such coating ranges from 2 to 20 weight percent of the cartridge case, corresponding to a calculated coating thickness of between about 3 and about 20 mils. For optimum protection against the deleterious effects of water penetration or absorption into the combustible cartridge case, the thickness of the coating ranges between about 10 and 15 mils. For maximum combustibility, the largest amount of RDX or other high energy explosive, consistent with the physical strength performance requirements of the coating, is employed. For RDX this amount is about 80 weight percent of the solids content of the coating composition. The coating solution should be carefully applied to provide a continuous coating free from breaks, pinholes, etc., over at least the exterior surface of the combustible cartridge case. Also, the novel coating can be used in conjunction with a light top- or undercoat of a resin of the aforesaid class containing no high energy explosive, whereby the water resistance of the case can be somewhat further improved in some instances.

Alkyl methacrylate polymers, such as the polymeric methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, and 2-ethylhexyl methacrylates are the preferred resins for use in the coatings of the present invention. The methyl-, ethyl- and butyl methacrylate polymers and mixtures thereof are particularly preferred for such use, since they combine excellent water and oil resistance, thermal depolymerization and consumability characteristics as well as excellent mechanical properties of the coating films produced, e.g., stability, toughness, hardness and adhesion to the case, as well as both physical and chemical inertness with respect to the nitrocellulose of the cartridge case. These properties are also possessed to a high degree by solid methacrylonitrile polymers and alpha methyl styrene polymers noted above; and such properties can be varied, as

desired, to a limited extent by choice of the nature and degree of polymerization of the resin employed. Further, thermoplastic polymeric resins of the aforesaid group on exposure to elevated temperatures can be substantially completely depolymerized to the monomer which is volatile under such conditions (N. Grassie, "The Chemistry of High Polymer Degradation Processes", Interscience Publishers, New York, N.Y., p. 4-5, 79 (1956)). By contrast, alkyl acrylate polymers, acrylonitrile polymers and styrene polymers, as well as other polymers including polyethylene, polypropylene, and polyisobutenes, thermally degrade to form large amounts of solid or tarry carbonaceous deposits and hence are not desirable candidates for the present application where complete removal of the polymeric resin binder without any remaining residue after combustion is desired for optimum non-metallic cartridge case performance characteristics.

Combustible, porous, fiber reinforced, nitrocellulose cartridge cases coated with the novel protective coating compositions of this invention, have been subjected to rigorous rain and humidity test cycles and then fired without leaving residue in the gun breech. Also, the solid high energy explosives RDX, HMX and PETN used in the coating are less sensitive to impact than liquid nitrate ester explosives, such as nitroglycerin and butanetriol trinitrate. This is important in processing and with regard to the safety of the coated cartridge during handling and transportation as well as under combat conditions. Further, liquid nitrate esters at ordinary temperatures migrate from a coating to the combustible cartridge case substrate; also, they volatilize therefrom at elevated temperatures and crystallize at sub-zero temperatures, thereby changing the ballistic properties of the coating. By use of the aforesaid solid explosives, which do not exhibit these deleterious properties of the liquid nitrate esters, the present invention provides coatings which possess stable ballistic characteristics.

The following examples serve to illustrate specific embodiments of the coated cartridge cases of the present invention. However, it will be understood that they are illustrative only and do not in any way limit the invention.

EXAMPLE 1

A liquid coating composition was prepared by dissolving 30 parts by weight of ethyl methacrylate polymer of high molecular weight and 0.91 inherent viscosity (sold under the trademark Elvacite 2042 by E. I. duPont de Nemours & Co.), and 10 parts by weight of butyl methacrylate polymer of high molecular weight and 0.53 inherent viscosity (sold under the trademark Elvacite 2044 by E. I. duPont de Nemours & Co.) in a mixture of 220 parts by weight of methylene chloride and 220 parts by weight of toluene. 160 parts by weight of standard RDX powder (97% passed through a No. 325 U.S. Standard Sieve) were dispersed in the resulting solution with agitation.

The liquid coating composition thus obtained was sprayed over the exterior surface of a 152mm porous combustible cartridge case, consisting of

- 8 weight percent of kraft fibers
- 26 weight percent of acrylic fibers
- 55 weight percent of nitrocellulose (12.6% N)
- 10 weight percent of polyvinylacetate resin binder
- 1 weight percent of diphenylamine stabilizer

to provide a substantially continuous coating over the exterior surface of the case, and allowed to dry.

Cartridge cases coated with the aforesaid coating composition and uncoated (control) cases, as well as cases coated with 100% of the aforesaid resin mixture (containing no RDX) were tested for water and oil resistance. The test procedures and results are set forth in Tables 1-4, and clearly show the marked decrease in the water and oil vapor transmission rates as well as liquid water and oil absorption obtained by means of the aforesaid protective coatings. The approximate coating thickness was calculated from the case surface area coated and the amount of non-volatile coating

Table 1 shows that when the part of the uncoated (control) cartridge case normally exposed to the moist atmosphere (i.e., the exterior surface of the case) was given a 12-13 mils thick coating of the aforesaid RDX/ethyl methacrylate-butyl methacrylate polymer system, the WVTR was reduced from 602 (average) g/24 hr/m² to 109 g/24 hr/m², and when the interior surface of the case was also similarly coated with the same system, the WVTR was reduced to 91 g/24 hr/m². A further improvement was obtained by applying a 1-3 mil topcoat of 100% of said methacrylate polymer resin over the RDX/methacrylate polymer coating (samples 6 and 7).

TABLE 2

Liquid Water Resistance of Treated and Untreated Cases*			
Sample	Protective Treatment (both sides coated)	Appropriate Thickness (per side) mils	% Liquid Water Absorbed by wt.
1	control	—	45.3
2	control	—	43.1
3	80 RDX/20 resin	12-13	1.89
4	ditto	13-14	1.99
5	100% resin	11-12	1.58
6	Same as 3 plus a < 1 mil topcoat of 100% resin	15-16 (includes topcoat)	1.37

*The cases were immersed for 24 hours under about 6 inches of water so that both the exterior and interior surfaces contacted the water.

TABLE 3

Oil Vapor Transmission Rates of Treated and Untreated Cases				
Sample	Protective Treatment (both sides coated)	Approximate Thickness (per side) mils	OVTR* g/24 hr/m ²	OVTR* g/24 hr/100 in ²
1	control	—	39	2.5
2	control	—	45	2.9
3	80 RDX/20 resin	12-13	19	1.2
4	ditto	13-14	19	1.2
5	100% resin	11-12	13	0.84
6	same as 3 plus 1-3 mil topcoat of 100% resin	15-16	13	0.84

*OVTR = Oil Vapor Transmission Rate, ASTM E 96-99, except that water was replaced by Aeroshell Fluid 60421 (petroleum base hydraulic fluid) marketed by the Shell Oil Company.

composition applied.

TABLE 1

Water Vapor Transmission Rates of Treated and Untreated Cases				
Sample	Protective Treatment	Approximate Thickness of Exterior Coat (mils)	WVTR* g/24 hr/m ²	WVTR* g/24 hr/100 in ²
1	control	—	584	38
2	control	—	620	40
3	exterior coat only	12-13	109	7.0
4	exterior & interior coats	12-13	91	5.9
5	exterior coat only of 100% resin (no RDX)	11-12	91	5.9
6	same as 3 plus 1-3 mil topcoat of 100% resin	12-13	73	4.7
7	Same as 6 plus inside coat	11-12	73	4.7

*WVTR = Water Vapor Transmission Rate, ASTM E 96-66

TABLE 4

Liquid Oil Resistance of Treated and Untreated Cases*			
Sample	Protective Treatment (both sides coated)	Appropriate Thickness (per side) mils	% Oil Absorbed
1	control	—	39.4

TABLE 4-continued

Liquid Oil Resistance of Treated and Untreated Cases*			
Sample	Protective Treatment (both sides coated)	Appropriate Thickness (per side) mils	% Oil Absorbed
2	control	—	40.5
3	80 RDX/20 resin	12-13	2.8
4	ditto	13-14	3.2
5	100% resin	11-12	2.8
6	same as 3 + 1-3 mil topcoat of 100% resin	15-16	2.2

*1 hour immersion under ½" of Aeroshell Fluid 60421, both exterior and interior surfaces exposed.

EXAMPLE 2

152mm combustible cartridge cases of the type described in example 1, whose exterior surfaces had been protected with a 12-13 mil coating of 80% RDX/15% ethylmethacrylate polymer/5% butylmethacrylate polymer, as described in example 1, were loaded with a standard propellant and fitted with a primer and a projectile. A number of the cartridges thus obtained were subjected to a simulated rain storm for 12 hours, totaling 8 inches of rain. The cartridges, both wet and dry, were fired from a 152mm cannon. The dry cartridges left no residue in the breech after firing, while the cartridges exposed to the rain left substantially no residue (a few harmless dust specks). Another group of the coated cartridges was subjected to a 10 day cycling, during each 24 hour period of which they were exposed for 16 hours to 105°F at 95% relative humidity and for 8 hours at 70°F at 95% relative humidity. These cartridges left no residue in the breech after firing. By contrast, cartridges made in the same manner from the same components but not provided with the aforesaid protective coating, left a substantial amount of residue in the breech, which had to be removed prior to firing the next round. U.S. Pat. No. 2,349,048 discloses the coating of a string of smokeless powder comprising nitrocellulose and nitroglycerin with a combustion deterrent coating of a high molecular weight polymethacrylate ester, and then cutting the string. The polymer coatings eliminate "hang fires" and are consumed during the combustion of the powder charge. The uncoated end surfaces permit the powder to be readily ignited by ordinary percussion primers even though the outer surface is coated with the methacrylate polymer, which is a very effective combustion retardant. The patent does not disclose the present invention, wherein a mixture of a methacrylate polymer and a high energy explosive like RDX is employed to coat the surface of a porous combustible cartridge case composed of nitrocellulose, reinforcing fibers and resin binder. Such coating does not function as a combustion deterrent

but serves to promote combustion of the coating and the case as well as protect the case against penetration of water and oil, whereby little, if any, residue remains in the gun when the cartridge is fired, even after exposure to water, and stable ballistic performance is achieved.

The foregoing disclosure is merely illustrative of the principles of this invention and is not to be interpreted in a limiting sense. We wish it to be understood that we do not desire to be limited to exact details of construction shown and described for obvious modifications will occur to a person skilled in the art.

What is claimed is:

1. A porous, combustible cartridge case comprising nitrocellulose, reinforcing fibers and a resinous binder, wherein at least the exterior surface of the case is covered with a substantially water-impermeable, consumable coating consisting essentially of finely divided particles of a solid high energy explosive of the group consisting of cyclotrimethylenetrinitramine, cyclotetramethylenetetranitramine and pentaerythritol tetranitrate, dispersed in a thermally depolymerizable, solid polymeric resin of the group consisting of alkyl methacrylate polymers, methacrylonitrile polymers and alpha methyl styrene polymers.

2. A cartridge case according to claim 1, wherein the coating contains between 30 and 90 weight percent of the high energy explosive and between 70 and 10 weight percent of the polymeric resin.

3. A cartridge case according to claim 1, wherein the resin is an alkyl methacrylate polymer.

4. A cartridge case according to claim 3, wherein the alkyl methacrylate polymer is a methyl methacrylate polymer, an ethyl methacrylate polymer or a butyl methacrylate polymer and mixtures thereof.

5. A cartridge case according to claim 3, wherein the alkyl methacrylate polymer amounts to about 20 weight percent and the solid high energy explosive is cyclotrimethylenetrinitramine and amounts to about 80 weight percent of the coating.

* * * * *

55

60

65