PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : F42B 12/80

A1

(11) International Publication Number: WO 92/08098

(43) International Publication Date: 14 May 1992 (14.05.92)

(21) International Application Number: PCT/US91/07844

(22) International Filing Date: 30 October 1991 (30.10.91)

(30) Priority data:
606,814 31 October 1990 (31.10.90) US

(71) Applicant: SAFETY SHOT LIMITED PARTNERSHIP [US/US]; 155 Alexander Street, Memphis, TN 38111 (US).

(72) Inventors: HUFFMAN, John ; 155 Alexander Street, Memphis, TN 38111 (US). SHANNON, John ; 1905 Ozark, Memphis, TN 38108 (US).

(74) Agents: KELBER, Steven, B. et al.; Oblon, Spivak, McClelland, Maier & Neustadt, Fourth Floor, 1755 South Jefferson Davis Highway , Arlington, VA 22202 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), LU (European patent), NL (European patent), PL, SE (European patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: ENVIRONMENTALLY IMPROVED SHOT

(57) Abstract

Environmentally improved alternatives to lead shot are provided that overcoat a lead core with a chemically inert polymer bonded thereto by heating lead shot coated with the polymer above the melting point of the lead shot, or by substituting for lead a combination of dense metal and light metal, and either a core/coating bimetallic sphere relationship or a matrix of light metal provided with powder of a heavy metal embedded therein. The composite shot exhibits a density similar to that of lead.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**ES**	Spain	**MG**	Madagascar
AU	Australia	**FI**	Finland	**ML**	Mali
BB	Barbados	**FR**	France	**MN**	Mongolia
BE	Belgium	**GA**	Gabon	**MR**	Mauritania
BF	Burkina Faso	**GB**	United Kingdom	**MW**	Malawi
BG	Bulgaria	**GN**	Guinea	**NL**	Netherlands
BJ	Benin	**GR**	Greece	**NO**	Norway
BR	Brazil	**HU**	Hungary	**PL**	Poland
CA	Canada	**IT**	Italy	**RO**	Romania
CF	Central African Republic	**JP**	Japan	**SD**	Sudan
CG	Congo	**KP**	Democratic People's Republic of Korea	**SE**	Sweden
CH	Switzerland			**SN**	Senegal
CI	Côte d'Ivoire	**KR**	Republic of Korea	**SU+**	Soviet Union
CM	Cameroon	**LI**	Liechtenstein	**TD**	Chad
CS	Czechoslovakia	**LK**	Sri Lanka	**TG**	Togo
DE*	Germany	**LU**	Luxembourg	**US**	United States of America
DK	Denmark	**MC**	Monaco		

+ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

Description

Environmentally Improved Shot

Technical Field

This invention is directed to substitute for conventional lead shot that will substantially reduce or eliminate the release of lead or similar toxins to the environment, or to animals ingesting the spent shot. The invention also pertains to a process for preparing that shot.

Background Art

It has long been known that lead shot expended, generally in hunting, that remains in the environment poses a significant toxic problem. The most severe problem presented by the spent lead shot is the ingestion by game fowl, particularly water fowl, of the spent shot for grit. Conventional shot, consisting or consisting essentially of lead, can lead to lead poisoning of the bird ingesting the shot. Estimates of water fowl mortality due to this type of lead poisoning ranges as high as 2 - 3% of all deaths per year.

These findings have generated a continual search for alternatives to conventional lead shot. Ultimately, steel (soft ron) shot was proposed as a substitute, as it is less expensive than more inert and softer metals (such as gold), resists erosion and produces no toxic effects when exposed to the acid environment of water fowl stomachs. Unfortunately, the cost of steel shot is higher than the cost of lead shot, and the steel is significantly harder than lead shot. As a result, steel shot can damage the barrels of most commercially available shotguns not designed specifically for shooting steel shot. Moreover, being substantially less dense than lead, steel shot is significantly inferior to lead, ballistically. This results in a high increase in the unnecessary loss of wild fowl due to crippling rather than kill shots. This increase has been estimated to be a higher increase in mortality than that due to lead poisoning.

Additionally, lead shot remaining in the environment is a source of lead introduced to the environment, that can be inadvertently included in a variety of food chains, not only water fowl. The natural acidity of rain fall, coupled with many acid environments, leads to leaching of the lead, and potential poisoning of important habitats and environments.

One alternative to conventional lead shot is discussed in U.S. Patent 3,363,561, Irons. As described therein, TEFLON is coated over lead shot, for the purposes of preventing lead poisoning. The process as described for coating the lead shot at column 3, lines 19-45 of the Irons patent, uniformly call for the application of TEFLON at temperatures only up to 400°F so as to avoid deformation of the shot which starts to lose its shape around 425°F. Polymers exhibiting the levels of corrosion resistance and abrasion resistance necessary to be effective in significantly reducing or eliminating lead leaching require temperatures in excess of 400°F to cure and bond satisfactorily. Most of the processes call for temperatures about 400°F. This results in a thin coating of polymer about an internal lead shot, but no significant bonding between the polymer and the shot. As a result, the polymer is easily peeled from the shot, and in fact, significant erosion or destruction of the polymer coating can occur in the mechanical environment of the shotgun barrel. Accordingly, this alternative has not received success in the industry.

It therefore remains a goal of those of skill in the art to provide ballistically acceptable, environmentally safe and lead erosion-free shot.

Disclosure of the Invention

This invention provides shot which yields no, or remarkably low, leaching of lead shot, according to established standards. These and other objects of the invention are achieved in a variety of embodiments.

As one preferred alternative embodiment, conventional lead shot is coated with a substantially inert, chemical and abrasion-resistant polymer, such as TEFLON,, or its fluorinated polymer variants. The TEFLON is baked in an environment which supports the shape of the lead shot, at a temperature above the melting point of the lead shot. This allows the polymer to be heated to the temperature required to optimally cure and bond the polymer without deformation occurring to the lead shot. Additionally, as the molten shot with the baked polymer coating is allowed to cool, there is an opportunity for mechanical bonding at the lead-polymer interface. As the molten shot with the baked polymer coating is allowed to cool, chemical as well as mechanical bonding occurs at the interface of the lead shot and the coating. As a result, the coating is substantially more adherent to the shot than prior art attempts, giving a dramatic reduction in lead leached from the shot under standard testing methodology.

In a second alternative, metals with a specific gravity greater than lead, particularly tungsten or depleted uranium (Udep) are provided with an outer coating of an alternative metal or metal alloy, such as zinc, bismuth, aluminum, tin, copper, iron, nickel or alloys, which when coated about the denser core, will result in an average density comparable to that of lead, e.g., 11.35. This process will also allow average densities of between 9.0 and 17.5 to be obtained which may be desirable for special applications.

In a third alternative, a molten preparation of a lighter metal, such as those mentioned above with respect to the bimetallic sphere embodiment, is provided with a powder of denser metals, such as tungsten or depleted uranium. As the melting point of tungsten is substantially above the melting points for all the metals and metal alloys mentioned, and the melting point for depleted uranium is above the majority of the metals and metal alloys mentioned, the resulting suspension can be formed into concentric spheres by conventional methods.

In these two latter embodiments, as the shot contains no lead, it cannot release any lead to the environment or animal ingesting the shot. Moreover, the majority of the alternative metals or metal alloys will yield a coating or matrix alloy that is sufficiently soft to be useful in conjunction with existing shotgun barrels. The density can be matched to that of lead, by proper adjustment of the concentration of the heavier and lighter metals.

Best Mode for Carrying Out the Invention

The shot that is the subject of this invention can be prepared in any dimension, and is desirably prepared in dimensions identical to that of current commercially offered lead or iron shot. Conventional shot is generally prepared by dropping molten lead or other metal preparation through a "shot tower". In this process, a preparation of molten metal is directed to a sieve positioned at a substantial height over a cooling bath, such as water or oil. As the molten metal, e.g., lead, falls through the shot tower, leaving the sieve, it naturally forms a sphere, and gradually cools in its passage down the tower, which may be as much as 120 feet or more. Finally, it is quenched in the cooling bath, which maintains the spherical shape of the shot.

In the first embodiment, providing lead shot with a mechanically and chemically bound inert polymer coating, shot prepared according to this method may be used. Conventionally prepared shot can simply be overcoated with a polymer coating, either including a solvent or solventless. Preferred polymers include fluorinated polymers such as TEFLON (polytetraflouroethylene) and related polyfluoro compounds offering superior performance values. These include using enhanced polymers, where the polymer either includes a secondary resin or includes a resin primer to improve adhesion. The coated shot is then embedded in a medium which provides uniform support to maintain the spherical shape of the shot, even if the shot itself becomes molten. A variety of substances can be used to provide the support beds. Preferably among support bed materials are casting compounds, fine silica or glass beads, gels, columns of air, and similar materials. The shot is raised to a temperature above the melting or deformation point of the shot itself. This allows the polymer to be heated to the temperature required to optimally cure and bond the polymer without deformation occurring to the lead shot. Additionally, as the molten shot with the baked polymer is allowed to cool, which cooling can be accelerated by air exchange, there is an opportunity for mechanical bonding at the lead-polymer interface. In the alternative, to prepare the coated shot, the atmosphere of the shot tower is provided with an aerosol fog of polymer. These aerosols are prepared according to conventional methods and do not constitute an aspect of this invention, per se. The molten lead droplets, as they exit the sieve fall through the fog and are coated with the polymer. The intrinsic heat of the molten droplets bonds the polymer to the shot as it is formed at the temperature required to optimally cure and bond the polymer. Additionally, as the molten droplets cool, there is an opportunity for mechanical bonding at the lead-polymer interface. The coated process can be enhanced by utilizing electrostatic spraying and coating techniques. This process has the advantage of coating the shot without introduction of separate processing steps. Thus, the shot is insulated from the environment, with an inert polymer which resists peeling or erosion.

To demonstrate the superior safety and lead leaching-resistance of the inventive shot, a series of comparisons were made, preparing shot coated with TEFLON available from duPont and similar fluorinated polymer available from Whitford under the name Whitford 1014, a resin enhanced fluorinated polymer, compared according to conventional procedures which call for baking of the polymer at 400°F for 20 minutes, as opposed to higher temperatures, as reflected in the graphs following. The shot so prepared was subjected to a variation of the standardized test for erosion rate, prescribed by Regulation, 50 CFR 20.134 (C) specifically referencing Kimball et al, Journal of Wildlife Management 35 (2), 360-365 (1971). Specifically, pursuant to the regulations identified, hydrochloric acid is added to each capped test tube in a volume and concentration that will erode a single No. 4 lead shot at a minimum rate of 5 mg/day. Test tubes, each containing either conventional lead shot or the inventive shot, are placed in a water bath on a stirring hot plate. A TEFLON coated magnet is added to each test tube, and the hot plate is set at 42°C and 500 rpm. Erosion of shot is determined on a daily basis for 14 consecutive days by analyzing the digestion solution with an atomic absorption spectrophotometer. The shot are all weighed at the end of the 14-day period to confirm cumulative weight loss. The 14-day procedure is repeated. Specific statistical analysis are required by the regulation. This variation is actually more severe than that prescribed by regulation.

As demonstrated by the foregoing comparative data, shot coated with an inert polymer according to the claimed invention exhibits superior erosion characteristics releasing substantially reduced amounts of lead, under standardized testing.

Pat018

gr5-1 -DuPont coating using conventional curing at maximum conventional temperature - 400 F. for 20 min.

day	control shot	gr5-1-1	gr5-1-2	gr5-1-3	gr5-1-4	gr5-1-5
1	899.2	610	647.8	775.3	569.3	784
2	814.9	852.1	763.3	879.3	733.2	897.8
3	763.5	748	719	727.5	711	771
4	533.3	549.7	615.4	626.5	551.1	479.6
5	709.9	735.1	747.9	736.3	776.8	785.4
6	791.6	779.9	840.1	671.6	806.3	748.1
7	666.9	776.5	719.9	641.7	741.1	821.5
8	711.1	731.9	755.9	775.6	795	763.2
9	918.2	833	878	861.5	862.8	802.9
10	774.4	838	892.4	836	867	817.8
11	706.4	780.5	849.1	791.5	840.6	898.1
12	791.4	924	878.3	695.9	901.6	851.3
13	764.6	831.7	860.9	463	687.1	723
14	600.1	822.9	791.8	813.7	900.2	892.3
total ppm	10445.5	10813.3	10959.8	10295.4	10743.1	11036.0
pct. of control		103.521	104.924	98.563	102.849	105.653
mean pct.				103.102		
median pct.				103.521		

Pat006-1

gr1-1 - DuPont coating using embedded curing at temperature above conventional - 400 F. for 20 min. then 625 F. for 20 min. (control ppm is projected and is believed to be low)

day	control shot	gr1-1-1	gr1-1-2	gr1-1-3	gr1-1-4	gr1-1-5
7	-	4.2	1.7	3.1	5.8	12
9	-	10	7	8	33	52
11	-	4.1	4.3	3.9	21.2	46.9
14	-	5	4	13	58	92
total ppm	5000.0	23.3	17.0	28.0	118.0	202.9
pct. of control		0.466	0.340	0.560	2.360	4.058
mean pct.				1.557		
median pct.				0.56		

Pat007

gr4-1 -Dupont coating using embedded curing at temperature above conventional - 400 F. for 20 min. then 625 F. for 20 min.

day	control shot	gr4-1-1	gr4-1-2	gr4-1-3
2	717	16	8	12
4	670	23.4	13.2	14.5
7	690	37	25	25
8	508.4	17.3	16.6	14.4
9	509.4	16.9	15.2	11.7
10	509	12.9	12.7	11.5
11	551.6	18.7	19.3	19.5
12	361.2	13.7	14.6	14.4
13	287.6	16	15	16.4
14	208	15.3	14.4	14.4
total ppm	5012.2	187.2	153.4	153.8
pct. of control		3.735	3.061	3.069
mean pct.			3.288	
median pct.			3.069	

Pat008

gr4-2 -DuPont coating using embedded curing at temperature above conventional - 400 F. for 20 min. then 625 F. for 20 min.

day	control shot	gr4-2-1	gr4-2-2	gr4-2-3
2	720	6	3	15
4	686	4.3	1.8	14.4
7	690	3	2	28
8	390.1	2	2.3	12.5
9	383.8	2.2	1.3	13
10	381.9	1.3	1.7	11
11	656.3	1.9	3.7	16
12	586.5	0.6	2	9.6
13	775.2	3	4	14
14	611.7	0.9	1.6	11.4
total ppm	5880.5	25.2	23.4	144.9
pct. of control		0.429	0.398	2.464
mean pct.			1.097	
median pct.			0.429	

Pat019

px4-1 - whitford coating using conventional curing at maximum conventional temperature - 400 degree F. for 30 min.

day	control shot	px4-1-1	px4-1-2	px4-1-3	px4-1-4	px4-1-5
1	831.2	194.2	696.1	365.3	697.9	424.1
2	814.6	712.1	823.5	829.9	847.7	766.5
3	861.2	806.2	785.9	842.3	819.3	859.7
4	771.6	783	704.6	753.6	691.8	731.4
5	704.8	817.8	759.8	731.1	820.4	810
6	640.8	714.2	647.3	766.5	758.7	673.2
7	772.6	777.5	761.1	551.6	786.7	770.5
8	718.6	480.8	758.6	552.9	498.1	803.3
9	957.8	455.3	984	937.8	483.3	441.8
10	806.1	406.6	915.3	805.9	879.7	856
11	1065	423.1	886.9	847.2	944.6	869.7
12	812.4	631.4	975	885.7	942.1	938.8
13	869.2	515.9	1021	1026	977.7	861.2
14	679.3	764.1	947.6	894.1	660.8	735.9
total ppm	11305.2	8482.2	11666.6	10789.9	10808.8	10542.1
pct. of control		75.029	103.197	95.442	95.609	93.250
mean pct.			92.505			
median pct.			95.442			

Pat009

px1-1 - whitford coating using conventional curing at maximum conventional temperature - 400 degree F. for 30 min.

day	control shot	px1-1-1	px1-1-2	px1-1-3
1	706.3	0.7	0.6	0
2	865.5	114.5	15.4	6.2
3	1250	270.8	31.3	7
4	745.4	689.3	157.4	20.5
5	734.1	616	182.4	31.3
6	457.4	699.9	275.7	55.6
7	600.8	711.2	478.7	111.4
8	666.7	680.8	524.6	179.3
9	599.2	648.1	624.6	207.9
10	582.9	682.9	680	316
11	660.9	692.5	606.4	434.1
12	654.2	789.7	778.5	767.5
13	936	931.9	922.1	915.8
14	598	598	705.2	593.1
total ppm	10057.4	8126.3	5982.9	3645.7
pct. of control		80.799	59.488	36.249
mean pct.			58.845	
median pct.			59.488	

Pat010

px1-2 - whitford coating using conventional curing at maximum conventional temperature - 400 degree F. for 30 min.

day	control shot	px1-2-1	px1-2-2	px1-2-3	px1-2-4	px1-2-5
1	1070	218	129.6	101.4	2.1	9.9
2	1140	457	258.4	431.5	5.4	12.5
3	10502	1122	933.6	1140	18.6	235.3
4	1068	1050	691.6	1150	27.3	1000
5	1023	1048	1067	1056	99.1	943.6
6	1115	1170	992.2	1133	214.2	1035
7	1100	1013	989.7	1032	360	1020
8	1040	1075	1050	1065	487.7	976.9
9	1170	1114	1109	1050	1025	1137
10	1050	1144	1080	1036	1042	1058
11	1094	1111	1096	1093	1004	1129
12	1130	1048	1121	1170	1092	1104
13	1015	824.5	758	1073	1010	728.7
14	964.3	904.1	955.1	953.7	915.8	933.9
total ppm	15029.3	13308.6	12231.2	13484.6	7303.2	11323.8
pct. of control		88.551	81.382	89.722	48.593	75.345
mean pct.			86.552			
median pct.			81.382			

Pat011

px3-1 - whitford coating using embedded curing at temperature above conventional - 450 F. for 10 min. then 625 F. for 6 min.

day	control shot	px3-1-1	px3-1-2	px3-1-3
1	736.3	0	0	0
2	821.7	0	0	0
3	1450	1.5	1.2	4.1
4	678.9	0.2	0	7.5
5	818.9	0	0	4.7
6	663.6	0.3	0	6.2
7	683.9	0	0	11.6
8	606.4	0	0	11
9	616.6	0	0	12
10	674.1	0	0	24.8
11	748.1	0	0	28.6
12	631	1.7	0	51.3
13	871.7	10.4	0.8	107.5
14	730.6	13.5	4.6	245.3
total ppm	10731.8	27.600	6.600	514.600
pct. of control		0.257	0.061	4.795
mean pct.			1.705	
median pct.			0.257	

Pat012

px3-3 - whitford coating using embedded curing at temperature above conventional - 450 F. for 10 min. then 625 F. for 6 min.

day	control shot	px3-3-1	px3-3-2	px3-3-3
1	900.6	0	0	0
2	729.1	0	13.8	0
3	704.9	0	16.8	0
4	714.5	0	18.6	0
5	715.3	0	21.5	0
6	684.8	0.5	24.5	0
7	752.2	2	23.9	0
8	627.8	5.7	40.8	0.3
9	848.4	9.8	52.2	18
10	1050	8.5	66.4	16.1
11	946.5	7.7	87.7	13.6
12	826.7	4.3	21.8	8.9
13	971.8	5.6	228.6	20.6
14	938.1	3.1	193.1	12.5
total ppm	11410.7	47.2	809.7	90.0
pct. of control		0.414	7.096	0.789
mean pct.			2.766	
median pct.			0.789	

Pat013

px6-1 - whitford coating using embedded curing at temperature above conventional - 450 F. for 10 min. then 625 F. for 6 min.

day	control shot	px6-1-2	px6-1-2	px6-1-3
1	775.2	0	0	0.5
2	611.7	0	3.5	1
3	740.1	0	11.6	0.7
4	714.1	0	20.3	1.7
5	706.2	0	26.1	8.9
6	584.9	0	28.8	19.1
7	904.7	0	42	10.1
8	939	0	35.9	14.4
9	747.7	0	52.6	20.1
10	844.1	0.3	52.3	13.6
11	614.3	0.9	82.3	19.1
12	715.6	1.7	136.9	21.2
13	744.7	1.1	204.4	20.7
14	718.8	3.2	282.3	29.9
total ppm	10361.1	7.2	979.0	181.0
pct. of control		0.069	9.449	1.747
mean pct.			3.755	
median pct.			1.747	

Pat014

px7-2 - whitford coating using embedded curing at temperature above conventional - 450 F. for 10 min. then 700 F. for 3 min.

day	control shot	px6-1-2	px6-1-2	px6-1-3
1	714.1	0.9	3.2	0
2	706.2	2.6	11.3	0
3	584.9	1.9	13.3	0
4	904.7	3.2	12.5	0
5	939	16.7	18.2	0.2
6	747.7	18.9	18.7	0
7	844.1	15.6	18.1	0
8	614.3	14.3	18.7	0.1
9	715.6	30.7	17.5	0
10	744.7	33.7	20.5	0.1
11	718.8	20.1	25.1	0.1
12	653.4	27	29.9	0.5
13	720.2	23.3	24.5	0.4
14	706.7	26.5	23.2	26.3
total ppm	10314.4	235.4	254.7	27.7
pct. of control		2.282	2.469	0.269
mean pct.			1.673	
median pct.			2.282	

Pat015-1

px7-3 - whitford coating using embedded curing at temperature above conventional - 450 F. for 10 min. then 700 F. for 3 min.

day	control shot	px7-3-1	px7-3-2	px7-3-3	px7-3-4	px7-3-5
1	669.2	2.5	0	0	0.3	0
2	843.6	2.2	0.4	0	0.3	0
3	945.3	10.2	0.8	0	4.3	0
4	1088	15.6	2	0.5	6.6	0
5	539.8	20.6	3.3	1.4	7	0
6	981.9	51.7	2	0.9	9.8	0
7	1025	32.2	48.6	3.3	8.4	0.1
8	1038	34.6	19.4	1.5	10.7	6.6
9	982.3	34.5	31.2	19.1	12.9	8.6
10	1010	44.1	38.1	20	16.7	15.6
11	769.1	42.3	39.8	8.5	14.8	9.8
12	1400	45.8	45.5	10.5	13.7	14.9
13	1211	46.1	57.1	9.3	11.8	18.8
14	994.7	54.1	99.7	10	16.2	27.8

total ppm	13497.9	436.5	387.9	85.0	133.5	102.2
pct. of control		3.234	2.874	0.630	0.989	0.757
mean pct.			1.697			
median pct.			0.989			

Pat016

px8-1 - whitford coating using embedded curing at temperature above conventional - 450 F. for 30 min.

day	control shot	px8-1-1	px8-1-2	px8-1-3
1	640.7	0	3	0.4
2	724.3	0.1	7.5	0
3	731.6	0	6.3	4.1
4	770.5	0	32.8	7
5	964.7	0	84.3	6.3
6	667.1	2.4	153.5	7.1
7	713.3	0.4	130.7	11.2
8	726.1	0.2	178.8	9.3
9	674.9	13	210.3	16.2
10	809.7	12.4	175.9	21.7
11	826.9	21	247.1	48.9
12	686	16.8	277.7	53.6
13	653.7	15.1	263.8	55.8
14	722	13.8	307.3	72.4
total ppm	10311.5	95.2	2079.0	314.0
pct. of control		0.923	20.162	3.045
mean pct.			8.043	
median pct.			3.045	

Pat017-1

px7-3 - whitford coating using embedded curing at temperature above conventional - 450 F. for 30 min.

day	control shot	px8-2-1	px8-2-2	px8-2-3	px8-2-4	px8-2-5
1	599.8	0	0	2.1	0	1.9
2	905.2	0	0	9.9	0	3.5
3	912.7	0	0	18.9	3.2	11.2
4	1014	0	0	29.9	2.2	13.6
5	534.5	0	0	25.9	2.5	10
6	1095	1.4	0.1	65.3	16.1	22.9
7	658.6	0.3	0.1	52.8	13.1	14.4
8	626.1	0.3	0.3	72.8	18.9	23.9
9	985.2	0.5	0.2	82.2	17.4	32.6
10	1050	0.6	0.2	89.4	26.1	35.8
11	945.4	0.4	0.5	108.6	36.6	58
12	1160	4.6	2.4	119.3	27.6	49.6
13	1099	6.8	10.4	135.3	37.9	69.8
14	977.9	34.5	44.6	167.3	35.3	94.1
total ppm	12563.4	49.4	58.8	979.7	236.9	441.3
pct. of control		0.393	0.468	7.798	1.886	3.513
mean pct.			2.812			
median pct.			1.886			

In alternative embodiments, lead is replaced as an element of the shot. In a first alternative, a core of a relatively dense metal, i.e., a metal with a specific gravity greater than that of lead, greater than 11.35, is overcoated with a less dense metal, which is not environmentally toxic. Among the metals that exhibit a specific gravity above 11.35, only uranium dep. and tungsten present realistic alternatives. The remaining alternatives are set forth in the following Table.

Pat004

METALS WITH SPECIFIC GRAVITY GREATER THAN LEAD - 11.35

Metal	Symbol	Specific Gravity	Melting Point C.	Rare or Precious	Radio-active	Pyro-phoric
Americium	Am	13.67	994	yes	yes	no
Curium	Cm	13.51	1340	yes	yes	no
Gold	Au	19.32	1064	yes	no	no
Hafnium	Hf	13.31	2227	yes	no	yes
Iridium	Ir	22.42	2410	yes	no	no
Mercury	Hg	13.55	-39	liquid	no	no
Neptunium	Np	20.25	640	yes	yes	no
Osmium	Os	22.57	2045	toxic	no	no
Palladium	Pd	12.02	1552	yes	no	no
Platinum	Pt	21.45	1772	yes	no	no
Plutonium	Pu	19.84	641	yes	yes	no
Protactinium	Pa	15.37	1600	yes	yes	no
Rhenium	zre	21.02	3180	yes	no	no
Rhodium	Rh	12.41	1966	yes	no	no
Ruthenium	Ru	12.41	2310	yes	no	no
Tantalum	Ta	16.65	2996	yes	no	no
Technetium	Tc	11.5	2172	yes	yes	no
Thallium	Tl	11.85	303	yes	no	no
Thorium	Th	11.72	1750	yes	yes	no
Tungsten	W	19.3	3410	no	no	no
Uranium(dep.)	U(dep.)	18.95	1132	no	no	yes

Among metals having a lower specific density than lead for use as metals that may be provided as the outer coating about the W or U dep. core are zinc, bismuth,, aluminum, tin, copper, nickel, iron or alloys made thereof. The proportion of core to coating will vary on the density of the metal forming the outer coating. If using tungsten as an example, if bismuth is selected, the tungsten will constitute 16.3% of the shot, while tungsten will constitute 52.1% (by weight) if the outer coating is formed of aluminum. As the core materials have extremely high melting points, 3410°C for tungsten and 1132°C for depleted uranium, the cores can be coated by conventional coating techniques, using metal or metal alloy baths, as described.

In a second non-lead containing alternative, the relatively light metals and alloys thereof described above are prepared in a molten bath and a powder of either W or U dep. is introduced thereto, creating a suspension of the denser metal in the lighter molten metal. This molten suspension may be formed into concentric spheres, again by a variety of methods, but most preferably, dropping through conventional shot towers, as lead shot is currently produced. Again, relative weights of the lighter and denser metals should be selected to give an average specific gravity equal to that of lead. In this respect, it should be known that selection of softer metals, such as tin, will give improved acceptability, although alloys made from any of the above-identified metals or the metals themselves, will be softer than the steel shot of the prior art.

This invention has been disclosed in terms of general descriptions, as well as reference to specific examples. Modifications and alternatives, particularly with regard to the identity of the chemically resistant polymer, ratios of metals, etc., will occur to those of ordinary skill in the art without the exercise of inventive faculty. These alternatives remain within the scope of the invention, save as excluded by the limitations of the claims appended hereto.

Claims

1. Ballistic shot comprised of a spherical core of lead provided with a coating of chemically resistant and abrasion-resistant polymer thereabout, said polymer having been applied to said lead core, said coated core then being heated above the melting point of the core, which allows the polymer to be heated to the temperature required to optimally cure and bond the polymer without deformation occurring to the lead shot, said molten shot with the baked polymer coating being allowed to cool for mechanical bonding at the lead-polymer interface.

2. The shot of Claim 1, wherein said polymer is a fluorinated polymer.

3. The shot of Claim 2, wherein said fluorinated polymer is polytetrafluoroethylene.

4. A method of making lead shot provided with a coating of chemically and abrasion-resistant polymer, comprising forming a spherical core of lead with a coating of polymer thereabout, supporting said coated core in a bed of shape-supporting material, heating said coated, supported lead to a temperature above the melting point of said lead sufficient to cure said polymer, and cooling said coated lead.

5. The process of Claim 4, wherein said lead core is first formed, and then coated with polymer.

6. The process of Claim 4, wherein said lead core is

formed by passing droplets of molten lead through a tower provided with an atmosphere of said polymer in aerosol form, said droplet being received in a quenching bath.

7. The process of Claim 6, wherein said droplet and said aerosol are provided with opposite electrical charges.

8. A lead-free shot, comprised of spheres of a dense metal selected from the group consisting of tungsten, depleted uranium and mixtures thereof, said core provided with a coating of lighter metal selected from the group consisting of zinc, bismuth, aluminum, tin, copper, nickel, iron and alloys thereof, said coating being selected such that the overall specific gravity of said coated core is between about 9.0 and 17.5.

9. A lead-free ballistic shot, comprised of a matrix of a light metal selected from the group consisting of zinc, bismuth, aluminum, tin, copper, nickel, iron and alloys thereof, particles of a heavy metal selected from the group consisting of tungsten, depleted uranium and mixtures thereof being embedded in said matrix, the relative weight of said powder and said matrix being selected such that the overall specific gravity of said ballistic shot is between about 9.0 and 17.5.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/07844

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): F42B 12/80
U.S.Cl.: 102/515

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	102/511,515,516,517,518,519 427/221,216 428/403,407 29/1.22,1.23

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4,027,594 (OLIN ET AL.) 07 June 1977	1-5
A	US, A, 4,714,023 (BROWN) 22 December 1987	1-5
A	US, A, 335,464 (LORENZ) 02 February 1886	1-4
A	EP, A, 10,845 (BANGOR PUNTA CORPORATION) 14 May 1980	1-5
X	US, A, 4,949,645 (HAYWARD ET AL.) 21 August 1990 See column 7, lines 42-52.	8, 9
X	US, A, 4,881,465 (HOOPER ET AL.) 21 November 1989 See column 3, lines 48-63.	8, 9
X	US, A, 4,498,395 (KOCK ET AL.) 12 February 1985 See column 2, lines 30-35, column 5, lines 37-46.	8, 9
X	US, A, 4,383,853 (ZAPFFE) 17 May 1983 See claim 1.	8, 9

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 February 1992	09 MAR 1992
International Searching Authority	**Signature of Authorized Officer**
ISA/US	for Michael J. Carone NGUYEN NGOC-HO INTERNATIONAL DIVISION Ngoc-Ho Nguyen

Form PCT/ISA/210 (second sheet) (Rev.11-87)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. [X] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. [ ] Claim numbers , because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. [x] Claim numbers 6 and 7, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

These claims fail to comply with the prescribed requirements because they do not add additional subject matter to claim 4. No meaningful search can be made since the claims as a whole are confusing.

3. [ ] Claim numbers__________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. [X] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-7 drawn to a lead shot coated by a particular process.

II. Claims 8 and 9 drawn to a lead free composite shot.

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. [X] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

[ ] The additional search fees were accompanied by applicant's protest.

[ ] No protest accompanied the payment of additional search fees.