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Task Order No. 0001, Information Search of Toxic-Free Ammunition addresses issues related to toxic and environmentally harmful effects caused by the use of some of the current small arms ammunition. The effort has consisted of looking at the theoretical aspects of replacing metallic lead and lead compounds in both service and training cartridges, as well as the current practice.

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This Document Contains Missing Page/s That Are Unavailable In The Original Document
68

Table of Contents

		Page
	Introduction	i
Section 1	Objectives of Toxic-Free Ammunition Survey	1
Section 2	Survey Approach	4
2.1	*What is Meant by "Toxic"*	4
2.2	*Regulatory Issues*	6
2.3	*Survey of Industry*	7
2.4	*Design of Toxic-Free Ammunition*	7
2.5	*Economic Implications of Candidate Materials*	7
2.6	*Resources Used to Perform Survey*	7
Section 3	Hazardous and Toxic Materials-Management and Policy Issues	9
3.1	*Policy and Regulations*	9
3.2	*Procedures and Infrastructure*	11
Section 4	Determining Criteria for Toxicity	14
4.1	*General*	14
4.2	*Lead*	15
4.3	*Barium*	15
4.4	*Bismuth*	16
4.5	*Antimony*	16
4.6	*Tungsten*	16
4.7	*Molybdenum*	18
4.8	*Copper Alloys*	18
Section 5	Characteristics and Availability of Candidate Metals	19
5.1	*General*	19
5.2	*Bismuth*	19
5.3	*Lead*	20
5.4	*Molybdenum*	20
5.5	*Tungsten*	20
5.6	*Steel/Iron*	21
5.7	*Copper and Alloys*	21

SAA

Section 6	**Responses to Questionnaires**	22
Section 7	**Design/Performance Issues for Toxic-Free Ammunition**	34
7.1	*General*	34
7.2	*Requirements Issues of Toxic-Free Ammunition*	35
7.3	*Performance Issues Imposed by International Convention*	36
7.4	*Penetration Comparison of Steel Core and Lead Core Ball Ammunition*	37
7.5	*Design and Ballistic Match of Toxic-Free 7.62mm Ammunition*	45
Section 8	**Recommendations**	52
Section 9	**Conclusions**	54

Appendices

Appendix I	**Toxicity of Tungsten and Bibliography - Summary from Danesi Report**	55
Appendix II	**Questionnaire - Information Search of Toxic-Free Ammunition**	75
Appendix III	**Bibliographies**	80

Introduction

Contract Summary Report
Contract DAAA-93-D-0001
Task Order No. 0002

Information Search of Toxic-Free Ammunition

Task Order No. 0001, Information Search of Toxic-Free Ammunition addresses issues related to toxic and environmentally harmful effects caused by the use of some of the current small arms ammunition. The effort has consisted of looking at the theoretical aspects of replacing metallic lead and lead compounds in both service and training cartridges, as well as the current practice.

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Section 1

OBJECTIVES OF TOXIC-FREE AMMUNITION SURVEY

There are four basic study objectives, as follows:

1. Investigate the Requirement in Detail, and Define "Toxic-Free"

One of the most fundamental requirements, and one of the most complex, is to determine what substances that may be used in ammunition components should be considered to be toxic. There are both medical and regulatory requirements, which are possibly in conflict with each other, and neither of these considers the effects on ammunition lethality in a quantitative way, so that performance tradeoffs can be made.

The distinct regulatory related criteria that need to be considered, are:

- ► The Department of the Army (DA) regulations refer to a specific EPA list which contains several hundred compounds. If we strictly interpret the regulations, according to the DA an item is considered toxic if and only if it is on this list. This particular list is small and relatively benign. Even lead is not on this list, although several lead salts are. No insoluble metals are on this list.

- ► At the other extreme, there is a master EPA list which contains over 70,000 substances. Everything is on this list.

- ► There are in-between criteria, as well as several useful handbooks that detail the effects and recommended exposure limits for a number of substances.

- ► The National Institute of Occupational Safety and Health (NIOSH) has published a list of substances that should be prohibited and/or monitored at the work place. This list is useful because it describes the effects of the various substances.

It is important to understand that many toxic substances may be acceptable if they enhance military effectiveness, and thereby reduce risks to troops. It is important to understand the tradeoffs between various levels of military effectiveness and the toxicity of materials that are necessary to achieve this effectiveness.

All of these issues need to be reconciled in order that we can generate a realistic understanding of toxicity and the effects of varying levels of toxicity.

2. Determine Status of Current Development and Production

The issue of eliminating and/or reducing the amount of toxic materials in ammunition is not new. Since a high percentage of small caliber ammunition is used in training, there have been several programs to develop training ammunition that did not use lead and was relatively non-toxic. In addition, several companies have developed lead-free primer formulations that may be useful. Some of the concepts that have been developed may have service applications. On the other hand, some of the concepts may involve the use of other toxic materials, and a detailed analysis is required.

3. Determine Progress of Ongoing Ammunition Research

It was felt that several organizations, both in the U.S. and overseas, have recognized the importance of this problem and looked into the development of toxic-free ammunition or ammunition components. In addition, it is possible that several ammunition concepts that were originally derived for other applications, such as training may, coincidentally, be less toxic than conventional small caliber ammunition. These concepts may be amenable to service use with some development. It is important to understand the status of ongoing research and development that may affect our ability to field non-toxic small caliber ammunition.

4. Delineate Possible Approaches to Toxic-Free Service Cartridges

There are many tradeoffs in the design and development of toxic-free ammunition. It is possible, for instance, to do a generic material tradeoff to determine the effects of bullet material properties (density, strength, ductility, etc.) on performance. The results can then lead to an approach. A more fruitful approach may be to look at material tradeoffs that have already been made and to note the lethality parameters that are associated with different material properties.

Section 2

SURVEY APPROACH

1. What is Meant by "Toxic"

The first issue to be resolved was the determination of what materials are toxic or, just as important, what materials need to be considered as toxic. All substances, and especially metals, are toxic to some extent at certain dose levels, and it is necessary to examine the relative toxicity in order that it can be related to potential usage and to weapon system performance. It is also important to note that the definition of toxicity is directly related to various regulations and to DA policy and definitions.

In order to determine how toxicity is viewed by the Army, we first focused on determining what current DA policy is, what structure is now in place to formulate and implement objectives, and what current laws, regulations, and procedures need to be implemented by DA. Relevant procedures for DoD agencies are contained in Part 32 of the Code of Federal Regulations. The specific procedures and regulations we are concerned with are contained in 32 CFR 650. This section then references various sections in Part 40, which contain EPA policy and regulations, including lists of the specific materials that are of concern.

However, this documentation is not necessarily complete in that it addresses primarily materials that have already been proliferated, or that it has been felt are likely to be proliferated. It is necessary to also refer to other sources to determine the relative toxicity of all materials we felt were likely to be considered for small caliber ammunition components. The first source was a report prepared by an AMCCOM Task Group[1] which compared the relative safety and lethality of depleted uranium

[1] Danesi, Michael E., "Final Report for the Kinetic Energy Penetrator Long Term Strategy Study," The AMCCOM Task Group, February 1990.

(DU) vs. tungsten penetrators. This was one of the first U.S. Army reports to indicate that tungsten, alloyed with other metals, could be a highly toxic material. It is in these alloyed forms that it might be used for small caliber ammunition. This report was also useful because of its very extensive bibliography, which is contained, along with a description of the toxicity of tungsten, in Appendix I, that led to other useful documentation. This documentation that was eventually used to determine relative toxicity, and was divided as follows:

1. Lists of compounds that have been identified by the EPA as toxic and/or as controlled with respect to release into the environment, as stated in the CFR's and other EPA derived sources.

2. Lists of compounds that have been identified by the National Institute of Occupational Safety and Health (NIOSH) as being toxic.

3. Several references that were located describing the results from indoor firing range tests.

4. Commercial handbooks that summarize toxicity data on soluble and insoluble compounds.

5. Reports from various medical journals

6. Material from the U.S. Department of Health, Education and Welfare (HEW).

7. Summaries from several private organizations such as the American Conference of Governmental Industrial Hygienists (ACGIH), The American Medical Association Industrial Medicine Specialty Group, and several foreign groups.

The final objective has been to look at the different materials that are generally used in ammunition components, and to focus on their relative toxicity. This has resulted in some controversy, since several organizations had already reached conclusions and have been designing ammunition that was supposed to be toxic-free. The problem may be that lead-free and toxic-free may have been taken to mean the same thing.

We felt that there was absolutely no question regarding the toxic effects of lead and lead compounds, and we tended not to emphasize this material. At the other extreme, several organizations have focused on tungsten as a substitute for lead, and very little concern has been shown for the potential toxic effects of tungsten by the small arms community. We therefore paid more attention to tungsten and other heavy metals, to be sure that we were not leading into making a substitution where the new material is not thought of as being toxic only because it has not yet been proliferated. Bismuth and molybdenum are other examples of such candidate materials, and will be discussed.

2. Regulatory Issues

The regulatory responsibilities and procedures that determine DA policy and its implementation are all outlined in 32 CFR 650, which defines the U.S. Army organization and infrastructure responsible for the protection and preservation of the environment in peacetime. DA is responsible, in one way or another, for implementing various parts of a number of laws (listed in Table 1), as they relate to the U.S. Army activities in peacetime, and there are various councils, committees and working groups that have been set up to implement and report on policy. In addition to the major army installations, the Offices of the Corps of Engineers and the Surgeon General have certain mandated responsibilities. An annual report, which is derived from inputs from major army commands and prepared by HQDA is due annually. An understanding of these regulations, policies, and procedures defines the relevant infrastructures at AMC and at HQDA. The approach that was used has been to compare the legislated organization and polices with the current organization and to have meetings with the cognizant individuals.

3. Survey of Industry

The information search was to survey industry, both in the U.S. and overseas. This was accomplished by mailing a questionnaire to likely industry sources for ammunition. A copy of the questionnaire is in Appendix II.

4. Design of Toxic-Free Ammunition

We looked at the overall ammunition system constraints and developed an approach to design a round that can function as a service as well as training round, and be as non-toxic as possible. This followed an investigation of the performance of two currently used 7.62mm cartridges as an example of what is possible in all small calibers. The performance of the M80 and M59 were compared in detail, since one contains much more lead than the other. Various design philosophies were adapted, and the performance of a possible all steel ammunition family that is ballistically matched to the M80 was considered. Although 7.62mm designs were used in this example, the methodology is useful at all calibers.

5. Economic Implications of Candidate Materials

There are three very important aspects of lead. It is cheap, it has a high specific gravity, and it has been proliferated in so many places that its use in ammunition represents only a minuscule part of the total world consumption. This is not true for other heavy metals, and data on consumption and cost, and other logistics issues (such as dependence on overseas sources) was thought to be very important.

6. Resources Used to Perform Survey

To the best of our knowledge, this survey is very unique, and several of the results are surprising. The research that was performed required documents from many diverse sources. The DA regulations, policies, and procedures were obtained from the CFR. The EPA regulations and lists of toxic substances and substances requiring dumping permits were also obtained from the salient sections of the CFR[2]. Many of the reports that were studied originated from the bibliography in the Danesi report that is in Appendix I. The main reference for tungsten is a study performed by NIOSH, and is published as NIOSH-77-127[3].

In addition, there are several general references that address issues relating to the toxicology of metals[4,5,6,7]. Sittig was found to be the most succinct, complete, and useful. This work covers all of the materials of concern, and it sums and cites recommendations of EPA, NIOSH, ACGIH, and other organizations. It also discusses various state regulations and applicable regulations from other countries, where they conflict with U.S. regulations. Appendix III contains reprints of several of the source lists that were used to perform this survey.

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[2] 32 CFR 650 "prescribes policies, assigns responsibilities, and establishes procedures for the protection and preservation of environmental quality for the Department of the Army in peacetime."

40 CFR 116 designates hazardous substances, and is referenced in 32 CFR 650 as the defining list for purposes of the Department of the Army.

40 CFR 140 designates

[3] National Institute for Occupational Safety and Health, "Criteria for a Recommended Standard - Occupational Exposure to Tungsten and Cemented Tungsten Carbide," Stanford Research Institute, September 1977.

[4] Sittig, Marshall, Handbook of Toxic and Hazardous Chemicals and Carcinogens, Third Edition, Noyes Publications, 1991.

[5] Clayton, George E. & Florence E. (ed), Patty's Industrial Hygiene and Toxicology, Third Edition, 1991, John Wiley and Sons, New York

[6] Izrael'son, Z. I. (ed), Toxicology of the Rare Metals, U.S. Department of commerce, National Technical Information Service (NTIS ACE-tr6710).

[7] Congress of the United States, Office of Technology Assessment, "Neurotoxicity - Identifying and Controlling Poisons of the Nervous System".

Section 3

HAZARDOUS AND TOXIC MATERIALS - MANAGEMENT AND POLICY ISSUES

1. Policy and Regulations

"The Department of the Army goal is to control hazardous and toxic materials to minimize hazards to health and damage to the environment"[8] is the stated objective of the Army Environmental Program. In order to achieve this objective:

a) "All material developed and procured by the Army is to be designed to minimize health and environmental hazards during research, development, testing, production, use, storage, and disposal."

b) DA will "limit, to the extent practicable, the use of toxic and/or hazardous materials, and employ procedures which provide maximum safety during storage, use, and disposal when less toxic or hazardous substitutes are not available."

c) It is necessary to "Develop safe and environmentally acceptable methods for the storage and disposal of materials which are inherently hazardous or potentially dangerous"

d) Finally, the Army needs to "provide properly trained personnel for the management, use, storage, and disposal of hazardous and toxic materials."

The materials that are considered "hazardous and toxic" from the point of view of DA regulations are defined by 40 CFR 116, which is a short list that has apparently not been updated for an extended period. It is interesting to note that a strict

[8] 32 CFR 650.122

interpretation of these regulations leads to the conclusion that insoluble lead is not a toxic substance. This is, of course, merely a regulatory nuance, and is in disagreement with an overwhelming preponderance of data and experience. The issue of what is and is not toxic is further complicated because there are numerous EPA lists of toxic substances. The DA is concerned, from a regulatory point of view, with Part 116 DESIGNATION OF HAZARDOUS SUBSTANCES, and a second list, Part 241 lists substances that are considered hazardous from a point of view of controlling dumping or disposal. At the same time, the master EPA list of toxic substances[9,10] contains over 70,000 compounds. From the DoD point of view only, a basic manual and periodic updates are available by subscription[11]

Although EPA is the principal DA contact point for compliance from a regulatory point of view, it is curious that the Federal Department of Health and Human Services (HHS) is not more involved. Although EPA is concerned with preservation of the environment, NIOSH which is a part of HHS, has responsibility for the protection of the workplace and has primary responsibility for determining how toxic a particular substance is to human exposure. NIOSH is also responsible for determining recommended exposure limits, that can then be implemented by OSHA. These NIOSH limits are significant, since we are interested in direct human exposure in addition to the effects on the environment. For instance, EPA is concerned with toxic pesticides, and is also concerned with various freon gases that may directly affect the environment even though they are not direct toxins. NIOSH would be concerned only with substances that are directly toxic hazards to humans.

DA policy is also affected by federal, state, and local objectives and regulations. There is no indication that DA is legally responsible for satisfying local or state regulations, but policy indicates that they shall be considered as objectives. Army authorities are required to cooperate with local authorities, to grant access to activities that may be responsible for pollution, and to report activities that may result in the release of pollutants and/or toxic substances. Liaison with other federal agencies is

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[9] Toxic Substances Control Act Chemical Substance Inventory: 1985 Edition

[10] Toxic Substances Control Act Chemical Substance Inventory: 1990 Supplement to the 1985 Edition

[11] DoD Hazardous Materials Information system: Hazardous Item Listing.

through the Corps of Engineers.

One issue of serious concern is that the substances that various agencies have been concerned with are those that either have already been proliferated (lead, asbestos) and those that they feel may be proliferated in the near future. For the case of toxic-free ammunition, we need to ensure that we are paying attention to the substitute materials as well as the lead we are trying to eliminate. The importance of this approach is illustrated by noting that at least three companies have developed "toxic free" ammunition using powdered tungsten alloys in place of lead, and that these organizations have chosen to ignore the fact that the various powdered tungsten alloys may actually be more toxic than lead. In several cases, bismuth has been considered as a potential substitute for lead, and it seems to have many of the same properties. Proponents of bismuth emphasize that it is not on the relevant EPA list of toxic substances, however this is probably because it has not been used in applications where it may be in close contact to humans - nor has it been introduced into the environment in significant amounts. It is important that we very thoroughly investigate any toxic effects of bismuth and other less proliferated materials before we use them.

2. Procedures and Infrastructure

The DA policy implemented by 32 CFR 650 creates a formal entity called the Army Environmental Program, which leads to an infrastructure and the subsequent assignment of responsibilities. The salient regulations[12] assign the Army Environmental Council the management responsibility to "review and redirect, as necessary, Army environmental policy and programs to ensure that the Army fulfills its responsibility under the National Environmental Policy Act and other Federal laws and regulations pertaining to pollution control and environmental protection." The Army Environmental Committee is the working group that supports the Army Environmental Council by proposing new programs and serving as a forum for the exchange of ideas and information; as well as assisting in the formulation of Army-wide implementing

[12] 32 CFR 650.7

instructions, in the resolution of interagency problems, and in maintaining surveillance over the ongoing Army Environmental Program activities. It is now believed that this infrastructure has been in fact replaced by the Senior Executive Environmental Council (SEEC)[13].

Other DA organizations are also involved in the environmental program. The responsibility for directing and coordinating environmental activities rests with the Chief of Engineers[14]. The Chief of Engineers also act as the liaison with local and state authorities, prepares any reports that are to be submitted outside DA and prepares the annual Department of the Army Environmental Quality Status Report as an input to the Annual Status Report on Environmental Programs and Activities, which will be discussed later. Of course, the Chief of Engineers also performs his traditional function of providing necessary technical and engineering assistance. The Office of the Surgeon General has the responsibility to "Monitor, evaluate, and disseminate data on health and welfare aspects of environmental pollution within the Department of the Army to ensure that the required degree of environmental enhancement is maintained."[15] The Surgeon General provides technical assistance, and is the office responsible for providing administrative determination regarding what is and is not toxic, and the degree of toxicity.

Using inputs from these organizations, Major Army commanders are required to "Establish an organizational structure to plan, execute, and monitor environmental programs."[16] Each commander is responsible for formulating and executing a program to ensure compliance with the Army's environmental goals. Army installation and activity commanders are to "Establish an organizational structure to plan, execute, and monitor environmental programs."[17] The installation commanders are to formulate and execute the operational plan, integrate the environmental plans into the

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[13] Conversation with Mr. Louis D. Walker, Deputy Assistant Secretary of the Army for Environmental Affairs.

[14] 32 CFR 650.7(c)

[15] 32 CFR 650.7(d)(1)

[16] 32 CFR 650.7(g)(1)

[17] 32 CFR 650.7(h)(1)

installation's basic mission, and to then report to major commanders the progress and effectiveness of the environmental programs and how they relate to the basic mission.

The inputs from Major Army commanders, Army Reserve commanders, and the National Guard commanders are furnished to HQDA-I&L (Installations and Logistics), and are used to prepare a yearly report, the Annual Status Report on Environmental Programs and Activities (RCS-DD-I&L (A) 1269[18]. This report describes the activities of the Army Environmental Program and details the activities of the major Army commands, the Reserves and the National Guard. The report also describes status of compliance with Federal/State standards and laws, the status of programs, estimates of the cost to bring facilities into compliance, and significant accomplishments to protect and enhance the environment while satisfying salient mission requirements.

[18] 32CFR 650.9

Section 4

DETERMINING CRITERIA FOR TOXICITY

1. General

There is an abundance of data that describes the relative toxicity of various materials and compounds. The master EPA list contains over 70,000 substances. This indicates that even the most innocuous substances are toxic under certain circumstances. It is possible to assume, from this list, that everything is toxic to some degree. Various other lists contain lesser numbers and go into different levels of detail regarding exposure limits and the effects of exposure. The matter is further complicated by the fact that some effects may not manifest themselves for a long period of time. For instance, it took over 100 years for people to realize how toxic lead actually is, and the Minimata tragedy in Japan illustrates how toxic mercury is and how long it took to recognize its effects. Therefore, since tungsten, bismuth, and molybdenum have been considered as potential candidate materials, it is extremely important that we understand their potential for toxicity at a very early stage.

As earlier mentioned, the Department of the Army regulations[19] state that a hazardous substance is defined by the list in 40 CFR 116. This is a regulatory list, and is certainly incomplete. Metallic lead, antimony and barium are not indicated on this list, but this certainly does not mean that they are not toxic. There are a number of more complete government and commercial sources that tabulate the toxic effects more thoroughly, and especially toxicity of the heavy metals[20,21].

[19] 32 CFR 650.123

[20] U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health; Recommendations for Occupational Safety and Health, Compendium of Policy Documents and Statements, January 1992.

[21] Sittig, Marshall, "Handbook of Toxic and Hazardous Chemicals and Carcinogens", Third Edition, Noyes Publications.

2. Lead

There is very little controversy to the declaration that lead in both inorganic (as a metal) and its various salts (also inorganic) are toxic. It is important that lead has been proliferated in solder used in plumbing, as a pigment in paints, as an ingredient in gasoline, as well as a common ammunition component. Lead is known to have both short-term and long-term effects, and is a cause of kidney, blood and nervous system damage. Lead is a cumulative poison that can build up in the body, and it can enter by inhalation, ingestion or directly through the skin. Long term exposure can lead to anemia, pale skin, decreased strength, nausea, paralysis, and permanent kidney damage. Ingestion of large amounts of lead can lead to permanent brain damage, seizures, coma, and death. There are several different time weighted average[22] (TWA) exposure limits that have been set. NIOSH has a TWA dust exposure limit of 0.1 $mgPb/m^3$, and a concentration in the blood of 0.060 mg/100 g of whole blood. OSHA has set a more stringent TWA limit of 0.05 $mgPb/m^3$. The lead salts, which are commonly used in primers, are also toxic and the various references discuss this. The relative toxicity seems related to the equivalent amount of inorganic lead that enters the body.

3. Barium

Barium and its compounds are of interest because they have been used as a substitute for lead salts in some primer compounds. Barium salts are not as widely used as lead salts, and actual experience with symptoms are less common. Barium is used as an alloying compound in metals, in pigments, as a pyrotechnic, in oil refining, and glass making. Due to the relatively low exposure, barium poisoning is essentially unknown in industry, although it is known that it can attack the heart, lungs, central nervous system, skin, and eyes. The OSHA and ACGIH limits for barium dust are both $0.5mg/m^3$.

[22] TWA concentrations are generally for up to a 10 hour workday, during a 40 hour workweek.

4. Bismuth

Bismuth is of interest because it has physical characteristics very similar to those of lead, and it appears to be far less toxic. Bismuth is used as an alloying compound to enhance machinability of various metals and in low-melting point alloys. There is currently no evidence connecting bismuth with industrial poisoning, however it has not been used as much as lead and other metals. It is not absorbed through the skin, and the only exposure has been with bismuth compounds used in medical procedures, such as the treatment of ulcers and other gastro-intestinal disorders. There is no federal exposure limit for inorganic bismuth.

5. Antimony

Antimony is currently a component of the lead alloy that is used in most small caliber ammunition, as well as lead alloys used for battery plates and other commercial applications. It is also used as an alloying component of steel and other metals. Antimony is considered to be a primary skin irritant, and to cause severe cardiovascular and heart effects. Liver and kidney degeneration can be the result of prolonged exposure. The ACGIH AND NIOSH exposure limits for atmospheric antimony are both set at 0.5mg/m^3 [23]. However, this metal is still controversial, and numerous states have set far more stringent limits and New Zealand has banned or severely restricted the use of antimony.

6. Tungsten

Tungsten is probably the most controversial of the heavy metals from the point of view of its toxicity. This is unusual because it has been used in industry and in consumer products for many years, and there is a great deal of data on its effects. Tungsten has been used as an ammunition component in armor-piercing rounds of all calibers, and several companies have made bullets of frangible tungsten, which is a

[23] Sittig, op cit

tungsten alloy powder bound in a plastic matrix. The express purpose of several of these rounds has been as a non-toxic training substitute for lead service cartridges. It is in this powdered form that it is an insidious toxin, and may actually be more dangerous than lead. Tungsten is most commonly used in the hard metal industry, as a component of cutting tools, and this is where much data has been gathered[24,25]

Tungsten, in its unalloyed, insoluble form causes transient or permanent lung damage and skin irritation. Occupational exposure to mixed tungsten dusts result in exertional dyspnea, coughing, weight loss, extrinsic asthma, pneumonitis, fibrosis, headaches, dizziness, nausea, and loss of the sense of smell. Tests in laboratory animals have resulted in epileptic-like seizures. Unlike lead, tungsten is deposited in the bone tissue and cannot be excreted by the body[26]. It has also been observed that breast cancer mortalities among the residents of tungsten mining areas in China, where over one half of the world's tungsten production is mined, are markedly higher than the national average.

The NIOSH TWA exposure limit for tungsten depends on the alloyed form. For pure insoluble tungsten this limit is 5 mg/m^3, however when tungsten is alloyed with 3% nickel, it goes down to 0.015 mg/m^3. Although tungsten has been an important industrial metal, and an important ammunition component for many years, there seems to be a dearth of quantitative data that can be used to assess the effects of the alloys of interest. Much of the available data is not consistent. It is clear that tungsten is a highly toxic substance, and its use in any situation where dust will be produced must be measured very carefully. Due to its potential use in frangible training ammunition, it is important to understand the potential danger to proliferating tungsten ammunition, and to monitor its use very carefully.

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[24] U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease control, National Institute for Occupational Safety and Health; "Criteria for a Recommended Standard... Occupational Exposure to Tungsten and Cemented Tungsten Carbide"; NIOSH-77-227.

[25] Bech, A. O., Kipling, M. D., Heather, J. C., Hard Metal Disease, British Journal of Industrial Medicine, 19, 139, 1962.

[26] Danesi, Michael E. (Task Leader), "Final Report for the Kinetic Energy Penetrator Long Term Strategy Study", Prepared for Mr. Michael F. Fisette - Assistant Deputy Chief of Staff for Ammunition.

7. Molybdenum

Molybdenum is another hard, dense metal that has been considered as suitable for ammunition components. Virtually all of the current supply is used as a metal alloying component in steel alloys, and as a component in lubricants. Its adverse effects are limited to transient irritation of the eyes and mucus membranes. In this respect, it would make a good choice for an ammunition material if we were concerned with the effects of the powder form. OSHA has set the TWA at 10mg/m^3.

8. Copper Alloys

Copper is currently used in a number of applications, including currency, electrical wiring, etc. It is not known to be toxic in its solid form, however the copper dust and mists are toxic, causing upper respiratory irritation. OSHA has set the TWA limit at 1mg/m^3. It would be prudent to consider the effects of a frangible copper training cartridge very carefully, and to plan adequate ventilation.

Section 5

CHARACTERISTICS AND AVAILABILITY OF CANDIDATE METALS

1. General

In order to consider the possible use of other metals as a substitute for lead, or as a component in a redesigned bullet, it is important to understand the cost and supply situation, as well as the properties that determine ballistic performance. Lead and steel are two of the cheapest metals available, and this is part of the reason why they are so commonly used. In order to replicate the aerodynamic and terminal ballistic properties of current ball ammunition we need materials that are close in density and strength. If we are to proliferate rounds that exhibit ballistic similitude with respect to the existing rounds, the materials we choose need to be fairly close in characteristics to the current materials. This is to make the redesign effort as simple and straightforward as possible. Several candidate materials have been investigated to determine relative cost, logistics considerations and availability[27].

2. Bismuth

Bismuth is a soft, heavy metal which is very much like lead in appearance, feel and properties. With a specific gravity of 9.8, it has approximately 83% of the density of lead. Bismuth, at approximately $2.50/pound, is substantially more expensive than lead. The main issue appears to be supply, since bismuth is currently available only as a by-product of the mining of copper and lead. There is only one domestic source of bismuth. In 1991, the U.S. consumed 1,427 metric tons, and imported 1,411 metric tons. It is felt that widespread substitution for lead is unlikely, due to the limited world supply. It is estimated that to replace lead with bismuth only in plumbing fixtures would require a doubling of the world supply. It is curious, however, that the Defense

[27] "Metal Statistics - The Statistical Guide to the Metals Industry", 85th Edition, Chilton Publications, New York 1993

Logistics Agency recently sold 91 metric tons from the national defense stockpile in 1992, retaining 740 metric tons.

3. Lead

Lead, with a specific gravity of 11.3, is one of the cheapest metals available, at approximately $0.35/pound. Mine production in the U.S. alone was over 1.1 million metric tons. The main use is in batteries and plumbing fixtures, and the amount used in ammunition is not sufficient to affect prices.

4. Molybdenum

Molybdenum is both dense and hard, with a specific gravity of 10.2, which is 90% that of lead. It is therefore a candidate ammunition material. Its primary industrial use is as an alloying material to strengthen steel and make it less susceptible to corrosion. Current price is about $3.35/pound. The supply is relatively elastic, and there does not seem to be a problem with supply.

5. Tungsten

Tungsten has a specific gravity of 19.3, and can be alloyed to be very hard. For these reasons it makes an excellent penetrator, and it has good aerodynamic properties. Both tungsten and tungsten carbide are currently used in anti-tank rounds as well as small caliber armor piercing rounds. Most tungsten is used in electrical equipment and in cutting tools. Most of the world's supply of tungsten comes from China and the domestic cost is driven by import duties, which are dependent on political considerations. The selling price, in the U.S. of the powdered metal is generally not quoted directly, but has been between $20 and $50/pound. The U.S. production of tungsten is solely in California and quantities are not available as they are considered proprietary to the two companies who are the only sources.

6. Steel/Iron

Another very important material is iron/steel. Steel has a specific gravity of approximately 7.8. When it is properly alloyed, it can be very hard. A properly designed bullet using steel in combination with a denser material to provide ballistic material can be very effective. Iron is indigenous to the environment and it rusts rapidly. It is therefore very friendly to the environment. In addition, if cleanup is required, it can be accomplished with a magnet. The U.S. production and consumption of steel are both very large, and the ammunition market is a very small part of total usage.

7. Copper and Alloys

Copper in pure form or alloyed with zinc (brass) or tin (bronze) is in wide spread use currently used in bullet jackets and cartridge cases. These alloys have a specific gravity of 8.9 and can be good ballistic materials. Cost is approximately $1.00/pound, and the supply situation is favorable.

Section 6

RESPONSES TO QUESTIONNAIRE

1. General

In order to ascertain what industry was doing in the area of toxic-free ammunition, a questionnaire was sent to a list of companies that are historically in the small arms marketplace. This included a number of overseas organizations. The results were not astounding. In the area of penetrator/bullet materials, the only significant work seems to be in the area of substituting another heavy metal (usually tungsten) for the lead in training ammunition. At least two companies are using a frangible tungsten/plastic material for training ammunition, and one company has designed a series of aluminum training rounds and they use tungsten powder ballast to ensure weapon function. It appears that the powder is then dispersed in the area of the gunner.

In the area of service cartridges, there is no known effort to replace lead, except in areas where other materials have traditionally been used (eg. armor penetrators). Several organizations are working on lead-free primers but, here again, we need to be careful to ensure that we are not substituting another toxic substance. At least one organization is replacing the lead salt with a barium salt that is also toxic.

2. Responses to Questionnaire

The organizations that were sent questionnaires are listed in the left column, and a summary of the response is on the right. A blank on the right indicates that no response was received.

Accudyne Corporation ATT: Mr. William Flaherty 340 N. Franklin Street Janesville, WI 53545	
Aerojet Corporation ATT: Marketing Department 1025 Connecticut Ave NW Suite 1107 Washington, DC 20035	Does not manufacture small caliber ammunition.
Alliant Techsystems ATT: Mr. Howard C. Healey 5901 Lincoln Drive Edina, MN 55436	They do not manufacture small caliber ammunition.
Amron corporation ATT: Mr. Richard R. Peters 525 Progress Avenue Waukesha, WI 53186	They produce metal parts for 20mm - 40mm cartridges and submunitions.
Applied Ordnance Technology, Inc. ATT: John S. Budzinski 103 Paul Mellon Court Suite A Waldorf, MD 20602	
Armtec Defense Products Co. ATT: Mr. Jack J. Alt PO Box 848 Coachella, CA 92236	They do not produce small caliber ammunition.
Ashot USA, Inc. PO Box 5554 New York, NY 10185	They indicate they can manufacture tungsten heavy metal projectiles that they claim will be cost competitive with lead projectiles. They did not furnish details.
Astra Holdings Corporation ATT: Richard W. White 8260 Greensboro Drive Suite 330 McLean, VA 22102	Their subsidiary, Kilgore, laps 20mm Phalanx and M50 series to US TDP.
Atlantic Research Corporation Att: Director of Marketing 5945 Wellington Road Gainsville, VA 22065	

Babcok & Wilcox
ATT: Mr. E. O. Hooker
PO Box 11165
Lynchburg, VA 24506

Barrett Firearms Manufacturing, Inc.
PO Box 1077
Murfreesboro, TN 37133

Battelle Columbus Operations
505 King Avenue
Columbus OH 43201-2693

Belcan Technologies, Inc.
ATT: Marketing Department
500 Sherbrooke Street W. #970
Montreal, Quebec
CANADA H3A 3C6

Blount, Inc.
ATT: Mr. Bob Bjerke
PO Box 856
Lewiston, ID 83501

They manufacture both lead-free primers as well as training cartridges. Their primers are probably the most advanced, from the point of view of being non-toxic, but do not meet military specs. They also have copper bullets and lead bullets that are completely sealed.

Bofors AB
ATT: Mr. Håkan Persson
1800 Diagonal Road
Suite 280
Alexandria, VA 22314-2850

British Aerospace, Inc.
ATT: Mr. Peter McLoughlin
1101 Wilson Blvd.
Suite 1200
Arlington, VA 22209

Calico Light Weapon Systems
ATT: Schuyler R. Graham, Jr.
405 E. 19th Street
Bakersfield, CA 93305

Chamberlain Manufacturing Corporation
ATT: Marketing Department
845 Larch Avenue
Elmhurst, IL 60126

CMS, Inc.
ATT: Mr. Edward J. White
4904 Eisenhower Blvd.
Suite 310
Tampa, FL 33634

Delta Defense, Inc.
1235 Jefferson Davis Hwy
Suite 710
Arlington, VA 22202

They manufacture a frangible tungsten/plastic round. They represent this round as having applications for training and limited service use. They purchase cartridge cases and lead-free primers.

Denver Research Institute
ATT: Mr. Larry L. Brown
2050 E. Iliff
Denver, CO 80208

Dyna East Corporation
ATT: Mr. Robert D. Ciccarelli
3201 Arch Street
Philadelphia, PA 19104

EMCO, Inc
Att: M.D. Blood
201 Industrial Parkway
Gadsden, AL 35903

They manufacture medium and large caliber ammunition components only.

Ensign Bickford Aerospace company
ATT: Mr. Robert J. Gilchrist
PO Box 427
Simsbury, CT 06070

ET Inc.
PO Box KK
Fairfield, CA 94533-0659

Expro Chemical Products, Inc.
ATT: Mr. Robert Brousseau
PO Box 5520
Valleyfield, Quebec
Canada J6S 4V9

They manufacture propellants, including propellants for small caliber ammunition.

Federal Cartridge Company
ATT: Marketing Director
900 Ehlen Drive
Anoka, MN 55303

Fiocchi of America, Inc. ATT: Mr. E.R. Oxsen Rt. 2 Box 90-8 Ozark, Missouri 65721	They have referred us to the parent company in Italy. Previous contact has indicated that they do manufacture lead-free primers, but they may contain other toxic materials.
FN Manufacturing, Inc. ATT: Mr. Willy Dumeunier PO Box 24257 Columbia, SC 29224	They manufacture small arms, but no ammunition.
General Ordnance Corporation 1640 W. Oakland Park Blvd. Suite 401 Ft. Lauderdale, FL 33311	
Hands Fireworks, Inc. 221 Nipissing Road Milton, Ontario L9T 1R3 CANADA	
Hanley Industries, Inc. ATT: Mr. Gaynor Blake PO Box 1058 Alton, IL 62002-1058	
Heckler & Koch, Inc. ATT: Mr. John N. Meloy 21480 Pacific Blvd. Sterling, VA 22166-8903	They do not manufacture ammunition. They suggested Royal Ordnance.
Hercules Aerospace ATT: Mr. Richard Schwartz Hercules Plaza Wilmington, DE 19894	They manufacture propellants only. They indicate that some propellants contain lead, and they are working on formulations that will replace these with lead-free formulations.
Hi-Shear Technology Corporation ATT: Mr. Don A. Novotny 24225 Garnier Torrence, CA 90505	
HITECH, Inc. ATT: Mr. Paul Bryan PO Box 3112 Camden, AK 71701	They do not manufacture small caliber ammunition.

Holston Defense Corporation
ATT: Mr. G. P. Gage
PO Box 1483
Kingsport, TN 37662-1483

They do not manufacture finished ammunition products.

ICI Explosives
ATT: Mr. Derek J. Crofton
PO Box 810
Valley Forge, PA 19482

IMI Services USA, Inc.
2 Wisconsin Circle
Suite 420
Chevy Chase, MD 20815

Jericho Precision Manufacturing Corporation
Att: Marketing Department
1 Lawton Street
Yonkers, NY 10705

Martin Electronics, Inc.
ATT: Mr. Roy B. York
Route 1, Box 700
Perry, FL 32347-9721

Mason & Hanger, Inc.
ATT: Mr. Jim Garnjobst
2355 Harrodsburg Road
Lexington, KY 40504-3363

New Mexico Tech
ATT: Mr. Herbert M. Fernendez
Campus Station
Socorro, NM 87801

NI Industries, Inc.
ATT: Marketing Department
5215 South Boyle Avenue
Los Angeles, CA 90058

They are a producer of large caliber ammunition.

Nico Pyroprecision, Inc.
ATT; Mr. Mark Fleiszer
1081 Ambleside Drive
Suite 710
Ottawa, Ontario
Canada K2B 8C8

They do not manufacture small caliber ammunition.

Nomura Enterprises, Inc.
ATT: Mr. Joseph A. Manna
2832 5th Street
Rock Island, IL 61201

Olin Ordnance
ATT: Mr. Albert J. Calabrese
St. Petersburg, FL 33716

Referred to East Alton

Olin Ordnance
Winchester Division
Att: Mr. J.D. Demaire
427 N. Shamrock
East Alton, IL 62024

Olin Corporation
ATT: Marketing Director
120 Long Ridge Road
Stamford, CT 06902

Olympic Load and Test, Inc.
ATT: Mr. Reed D. Copsey
547 Diamond Point Road
Sequim, WA 98382

Orlando Technology, Inc.
ATT: Jerry D. Abrams
PO Box 855
Shalimar, FL 32579

Pacific Scientific Co.
Energy Dynamics Division
ATT: Mr. Thomas Walsh
Box 5002
Chandler, AZ 85226-5111

Physics International Co.
ATT: Mr. Emil Seaman
PO Box 5010
San Leandro, CA 94755-0599

Pyrotech International, Inc.
ATT: Mr. Gary A. Fadorsen
PO Box 206
Macedonia, OH 44056-0206

Pyrotechnic Specialties, Inc. ATT: Mr. Jerry D. Hall RR2, Box 733 Byron, GA 31008-9412	
Quantic Industries, Inc. ATT: Mr. Robert M. Valenti 990 Commercial St. San Carlos, CA 94070	No ammunition manufacture
Rheinmetall GmbH/Rheintech, Inc. ATT: Marketing Director 2000 Corporate Ridge Drive Suite 515 McLean, VA 22102-7854	
Safety Consulting Engineers, Inc. ATT: Mr. C. James Dahn 2131 Hammond Drive Schaumburg, IL 60173	
SIGARMS, Inc. ATT: Mr. David A. Flanders Corporate Park Exeter, NH 03833	They do not manufacture ammunition.
Small Arms Development & Testing Co., Inc. ATT: Mr. Bruce W. Seiler 123 Summit Lane Bala Cynwyd, PA 19004	
SNC Industrial Technologies, Inc. ATT: Marketing Director 5, Montee des Arsenaux Les Gardeur, Quebec J5Z 2P4 CANADA	They requested additional data on our contract and relationship with ARDEC. A final reply has not yet been received. Discussions indicate that they make training ammunition using frangible or powder tungsten, and it appears that the powder exits the barrel.
SNPE ATT: Mr. Bernard Zeller 1111 Jefferson Davis Hwy Suite 700 Arlington, VA 22201	They do not manufacture small caliber ammunition, and they have forwarded inquiry to Giat. (We had independently sent an inquiry to Giat.)
Sturm, Ruger & company, Inc. ATT: Mr. James P. Cowgill PO Box 2009 Springfield, VA 22152	

Stresau Laboratory, Inc.
ATT: Mr. James C. Graber
PO Box 368
Spooner, WI 54801

Talley Defense Systems, Inc.
ATT: Mr. William W. Mogan
3500 North Greenfield Road
Mesa, AZ 85205

They do not manufacture small caliber ammunition.

Talon Manufacturing Company, Inc.
ATT: Mr. Larry S. Thompson
HC71, Box 130AA
Hickory Corner Road
Augusta, WV 26704-9524

Verbal data indicates that they manufacture plastic training ammunition in various calibers.

Technical Ordnance, Inc.
ATT: Mr. John C. Yuhas
PO Box 800
St. Bonifacius, MN 55375-0800

They are currently developing a lead-free primer. They have not supplied details. They expect costs to be identical with current primers.

Trojan Corporation
ATT: Mr. Tom M. Clark
PO Box 310
Spanish Fork, UT 84660

Western Cartridge Company
East Alton, IL 62024

Wetherly, Inc.
ATT: David E. Boyd, Jr.
1100 Spring St. NW
Suite 800
Atlanta, GA 30309

Whittaker Ordnance
ATT: Mr. Michael Todd
2751 San Juan Road
Hollister, CA 95023

Winchester Repeating Arms Company
New Haven, CT

Director of Marketing
Direccion General de Fabricaciones
Militares
Cabildo 65
Buenos Aires
ARGENTINA

Director of Marketing
Department of Defence
Office of Defence Production
Anzac Park West Offices
Canberra ACT 2600
AUSTRALIA

Small Arms Ammunition Factory No. 1
Footscray, Victoria
AUSTRALIA

Director of Marketing
Companhia Brasileira Cartuchos
Av Industrial 3330
PO Box 51
09000-Santo André-SP
BRAZIL

Dominion Arsenal
Industries Valcartier, Inc
Valcartier, Quebec
CANADA

Haerens Ammunitionsarsenalet
Copenhagen
DENMARK

They do not manufacture toxic-free ammunition.

Armeria de Fuerzas
San Cristobal
DOMINICAN REPUBLIC

Etablissements Luchaire S. A.
ATT: Marketing Director
180 Boulevard Haussmann
75382 Paris Cedex 08
FRANCE

Nitro-Nobel AB
GYTTORP
F-71382 Nora
SWEDEN

They do not manufacture finished ammunition.

Dynamit-Nobel AG
Postfach 1261
Kaiserstrasse I
D-5210 Troisdorf
WEST GERMANY

Dynamit-Nobel Wien GmBH
Postfach 74
Opernring 3-4
A-1015 Vienna
AUSTRIA

Hellenic Arms Industry SA
ATT: Marketing Director
160, Kifissias Ave.
115 25 Athens
GREECE

Referred inquiry to Greek Powder & Cartridge.

Greek Powder & Cartridge S/A.
ATT: Marketing Director
1, Ilioupoleos Ave
172 36 Hymettus
GREECE

Director of Marketing
Poongsan Metal Corporation
Keuk Dong Building
60-1, 3 Ka Chungmu-Ro
Chung-Ku
CPO Box 3537 Seoul
REPUBLIC OF KOREA

Director of Marketing
Pakistan Ordnance Factories
Wah Cantt
PAKISTAN

Director of Marketing
Industrias Nacionals de Defesa, EP
Rua Fernando Palha
1899 Lisboa Codex
PORTUGAL

Director of Marketing
Chartered Industries of Singapore
Pte Ltd.
249 Jalan
Boon Lay
SINGAPORE 2261

SAA

Director of Marketing
Empresa Nacional 'Santa Barbara'
Manuel Cortina No. 2
Madrid 28010
SPAIN

Director of Marketing
Vammaskoski Works
PO Box 18
SF-38201 Vammala
FINLAND

They do not manufacture small caliber ammunition.

Eurometaal NV
Postbus 419
1500 EX Zaandam
THE NETHERLANDS

Giat Industries
Att: Marketing Director
7 Route de Guerry
Bourges 18023
FRANCE

They manufacture both training and service cartridges. Training cartridges use copper or tin powder in a plastic matrix. They also make lead core bullets and completely encapsulate the lead using either metal or plastic. They purchase lead-free primers.

NMW de Kruithoorn B.V.
PO Box 1080
5200 BC 's-Hertogenbosch
THE NETHERLANDS

They do not manufacture small caliber ammunition.

Section 7

DESIGN/PERFORMANCE ISSUES FOR TOXIC-FREE AMMUNITION

1. General

There are several approaches to the design of toxic-free ammunition. The most straightforward is to look at materials that have the desired physical properties and are not known toxins or carcinogens. In order for a bullet to maintain the maximum possible energy in flight, and to simultaneously exhibit superior terminal ballistic effects, we need the bullet material to have a high average specific gravity. Lead has traditionally been the material of choice for ball ammunition because it is dense and cheap, yielding unique ballistic characteristics. This is where the conflict arises - lead and other heavy metals are, for the most part, toxic and most substitute metals are also considerably more expensive than lead. Of all the materials we have looked at to replace lead, it seems that the only one that is truly toxic-free, has adequate terminal ballistic performance, and can be available in quantity and at reasonable cost is steel. This section, therefore, focuses on an obvious solution - the issues and constraints involved in the use of steel for small caliber service cartridges.

The issue of primer materials is also important. The current primers also use lead in the form of lead salts. Primer design has evolved over the years, and virtually all current primers use lead styphnate, and exhaust lead, barium, and antimony as products of combustion. These primer formulations seem to be the most satisfactory from the point of view of sensitivity, lack of corrosive properties, and aging characteristics. We know of at least two efforts to modify the primers to make them less toxic. In one case (Fiocchi), the lead byproducts have been removed, but barium remains. In the Blount primer[28], the primary effluent is potassium, which is theoretically less toxic. Here again, this relative toxicity needs to be re-examined very

[28] U.S. patent No. 4963201

carefully before a decision to proliferate a new primer composition is made.

It is also significant that neither of the new primer compositions is capable of meeting the requirements of MIL-P-46610E, and further development work is needed.

2. Requirements Issues of Toxic-Free Ammunition

In order to understand the complete design problem, we need to consider a wide range of issues that relate to logistics, effectiveness and life-cycle cost, as well as relative toxicity. It is especially important that any degradation in performance be kept to an absolute minimum, and be well understood. From a practical point of view, it is also clear that existing stocks of ammunition will not be thrown away, and it will take a long time for the production base of any non-toxic replacement round to reach the level where continued production of the current round is no longer necessary, if this ever occurs. This implies that any replacement round must ballistically match the current round(s).

The life-cycle costs for an ammunition family are more complicated than simply the cost involved in manufacture and distribution. The entire ammunition system life-cycle cost includes range and battlefield clean up of toxins, if this is deemed necessary. As a result, a non-toxic round which has a higher per item procurement cost may be, in the long run, less expensive to use than the existing lead based round. Manufacturing cost projections are also made very difficult in that current material costs may eventually differ significantly from future material costs if world-wide supply and demand relationships are upset by high volume production of this new type of ammunition. Therefore, that which appears to be cheaper or more expensive today based on a superficial examination of the market, may actually be in the future more or less expensive, given these marketplace adjustments.

Performance requirements of toxic-free (or any other) ammunition which must be considered when determining its suitability include: 1) soft (human) target lethality effects; 2) penetration of helmets and body armor; 3) anti-material (thin metal and ballistic fabric) effects; 4) effective range and accuracy; 4) ballistic match to current rounds; 5) safety; and 6) restrictions imposed by international conventions. The development of a non-toxic service round presents a significant, yet surmountable, challenge with respect to these performance requirements. If, however, the intent of the non-toxic ammunition is to be a substitute for the use of toxic ammunition in training alone, compromises in all of these performance requirements except safety may be relaxed depending on the objectives of the training ammunition. Relaxing training ammunition requirements may offer the opportunity to develop a suitable round faster and at lower cost, although this possibility has not been considered in this survey.

3. Performance Restrictions Imposed by International Conventions

This issue has been brought to the front of the discussion so that it can be resolved without detracting from the technical merits of any of the toxic-free concepts to be presented. We have, in the past, performed extensive research in the lethality effects of small arms ammunition, and this research inevitably involved issues of inhumane weapons and aspects of the Stockholm Convention to which the United States is a signatory. Briefly summarized, the primary concern is that the bullet perform such that it does not extensively mushroom and shatter into many pieces within the body, and that it does not tumble as it penetrates. The worry with these types of bullets is that they create a very large and perhaps unnecessarily destructive bullet wound tract. In practice, traditional lead core bullets are required to have a full metal jacket to restrict mushrooming and fracture to the minimum extent possible to ensure high and reliable lethality (e.g. no hollow points, jacketless lead ball rounds, or exploding projectiles). Copper has been the material of choice for bullet jackets. However, copper clad steel is also used as a jacket material.

Ensuring that the bullet does not tumble during penetration requires specific attention to the spin rate and mass properties of the bullet, and its fluid dynamic behavior while penetrating human tissue.

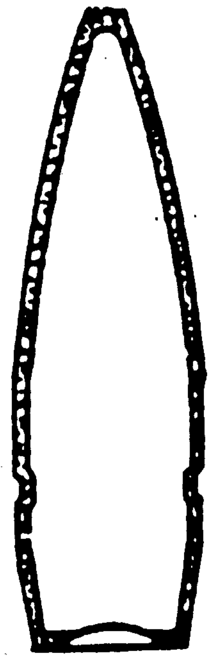
There are many ways to respect these aspects of international conventions. Although certain specific designs are accepted by convention, alternate designs which achieve the same equivalent lethality effects, while using alternate materials, should receive no credible objections. A detailed study of bullet design principles as related to maximizing wound ballistic effects will be necessary when considering alternate materials, however, there does not seem to be any reason to believe that this will be a driving issue.

4. Penetration Comparison of Steel Core and Lead Core Ball Ammunition

Standard service 7.62mm ball ammunition is exemplified by the M80 projectile, shown in Figure 1. Its core is a lead-antimony alloy, and is the primary toxin of concern. Due to its use in ammunition, lead-antimony has also been considered a material of strategic military importance, and there has been concern about its availability during time of war. For this reason, small arms ammunition has also been designed to use less lead based material in the bullet core. One example of this is the M59 ball round, shown in Figure 2, which replaces most of the lead core, by volume and weight, with a mild steel core. Under these circumstances, we will show that the performance did not degrade, and may actually improve against many targets. The steel, therefore, becomes a logical non-toxic candidate to substitute for lead in ball ammunition.

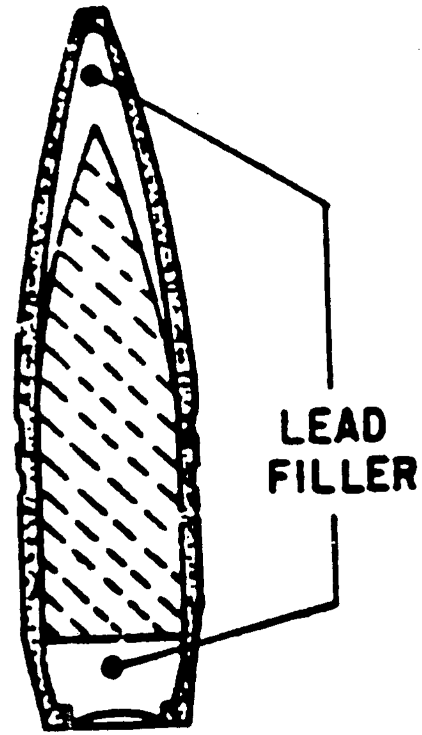
It is fortuitous that both the M80 and M59 have been extensively tested against a variety of targets, and this test data is conveniently available online using the SAA AADS data base. We have therefore investigated both quantitatively and qualitatively whether there appear to be any indication of terminal ballistic performance disadvantages to using steel as a replacement for a portion of the lead in the bullet core. Five targets of interest were investigated for which AADS comparison V50 data existed for both of these projectiles: Rolled Homogenous Armor (RHA), High Hard Armor (HHA), 2024-T4 aluminum, woven fiber glass fabric (WRF), and 16 ounce per square yard per ply Kevlar. As a footnote, both the M80 and M59 have the same muzzle velocity and ballistic coefficient, and are considered to be ballistically matched (see Table 1). Therefore, straight V50 comparisons are valid without the need for range-velocity corrections.

Figure 1



7.62mm BALL M80

Figure 2



7.62mm BALL M59

7.62mm BALL M80		7.62mm BALL M59
1.140	LENGTH	1.28
0.309	DIAMETER	0.309
149	WEIGHT (gr)	151
GM/CS	JACKET MAT'L	GM
38	JACKET WEIGHT	57
Pb	CORE MAT'L	STL/Pb
111	CORE WEIGHT	55/39

(a) Metallic Target Performance Comparisons

For RHA plate up to 3/8ths of an inch thick, regardless of obliquity, both the M80 and M59 have essentially the same V50. (See Figures 3a,b,c.) As RHA targets become thicker and more vertical up to a maximum of 1/2 inch at zero degree obliquity, the M80 shows a slight edge, requiring only 3000 fps for the vertical 1/2 inch target as opposed to 3500 fps for the M59 round (both greater than normal muzzle velocity). Since both bullets effectively weight the same, a plausible explanation for the reduced normal impact effectiveness of the M59 is the inhomogeneity of the bullet near the tip with its highly pointed nose on the steel core coupled with the thin layer of lead filler. Whereas the entire bullet mass of the M80 will uniformly flatten out and contribute to penetration against the normal target, the lead filler mass forward of the steel core in the M59 will be dramatically displaced radially upon impact. The steel core will resist flattening out and the lead filler will be dispersed and not deposit its energy into the target. At oblique impact, however, these design difference have less impact on penetration efficiency, since some tip filler in the M80 will also tend to be wiped away and not contribute to penetration. However, the muzzle velocity for these rounds is just under 2800 fps. In addition, true normal impact against any armored target is rare in actual combat. Therefore, within the realistic range of impact velocities and target orientations, there appears to be little difference in performance between the M59 and M80 against RHA, and only very close to the muzzle, which is a highly unlikely engagement range in actual combat.

Against high hard armor (HHA) (Figures 4a,b,c), however, the steel core M59 shows a slight advantage over the M80. At muzzle velocity, HHA targets which can be penetrated by both bullets range from 1/8th inch at 60 degrees obliquity to 1/4 inch vertical. At 60 degrees obliquity the M59 requires approximately 200 fps less than the M80, but effectively the same V50 at normal impact. Clearly, both rounds are about half as effective against HHA as against RHA. However, the penetration resistance of the HHA is disrupting the homogenous lead core M80 to a greater extent than the loss of the lead filler in the steel core M59. Steel mild appears to be a more efficient penetrator against the hard armor.

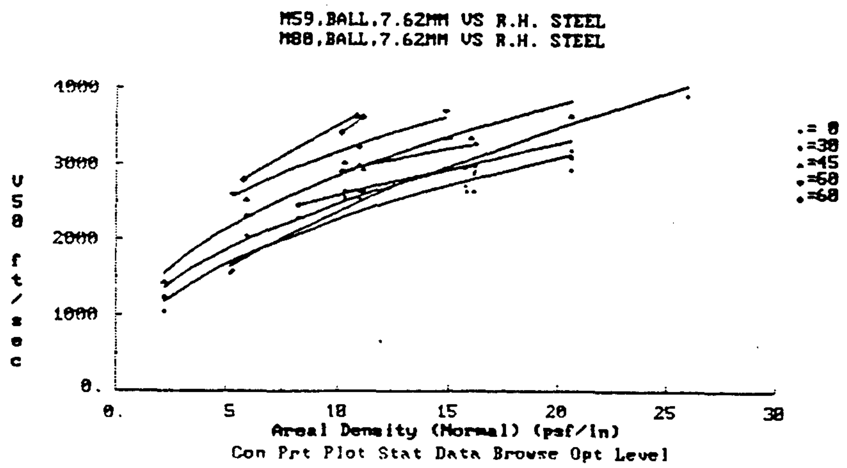


Figure 3(a)

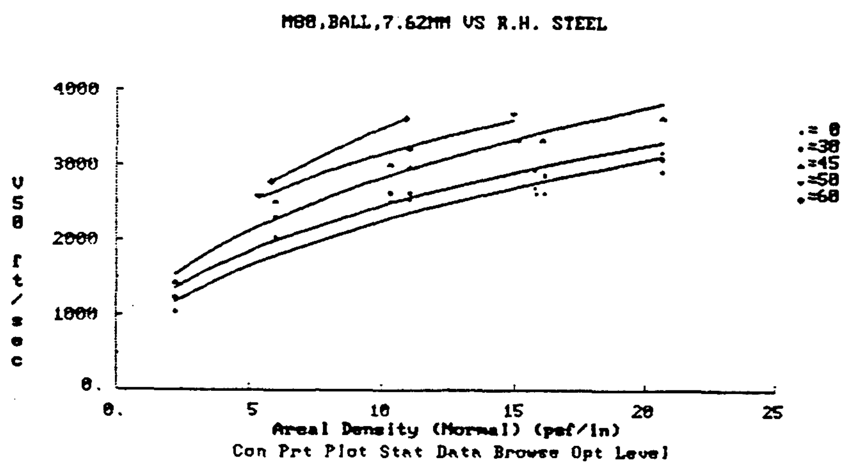


Figure 3(b)

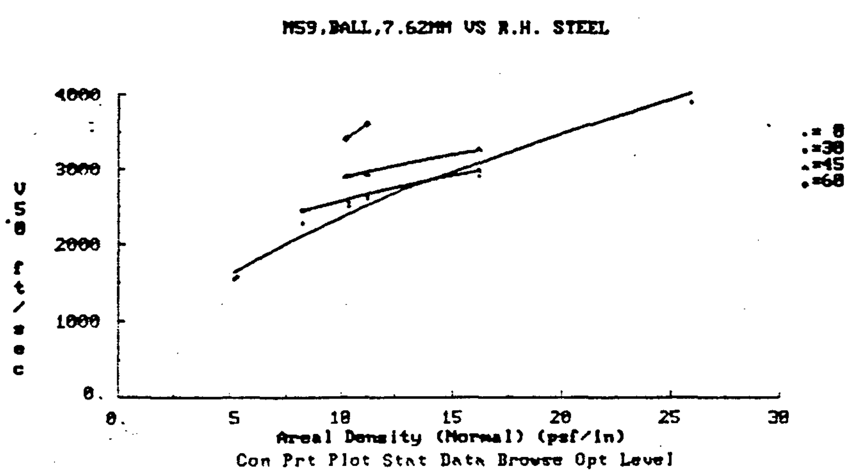


Figure 3(c)

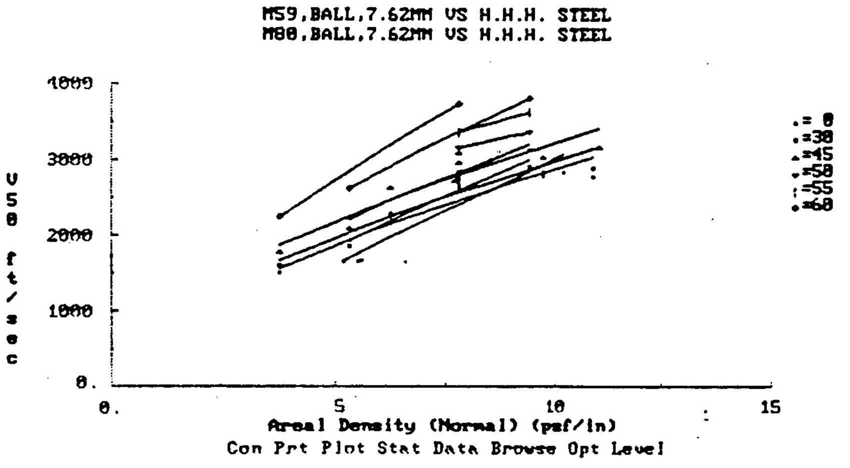


Figure 4(a)

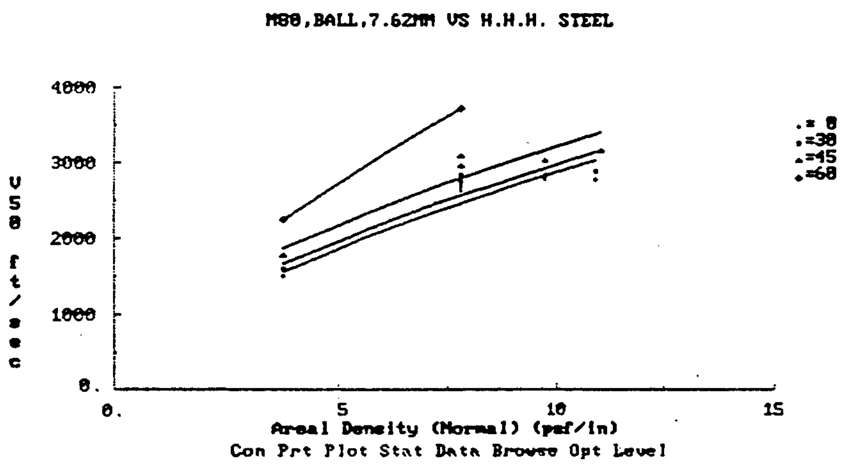


Figure 4(b)

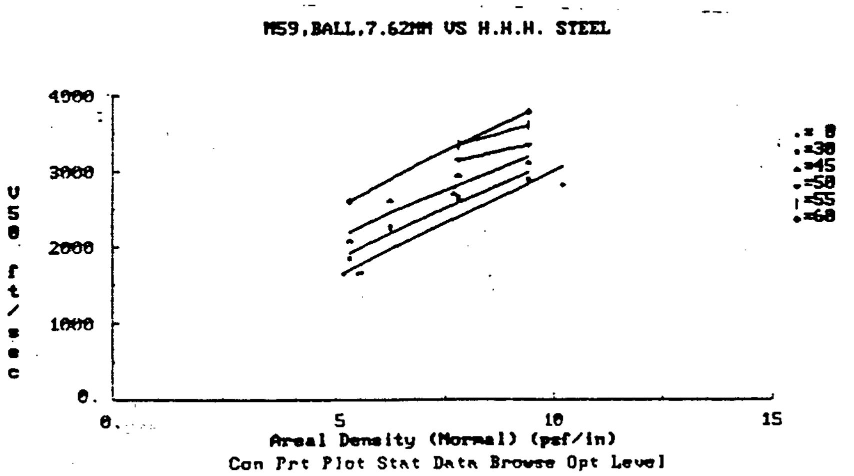


Figure 4(c)

Against typical aluminum armor, such as 2024-T4 (Figures 5a,b,c), the steel core M59 performs somewhat better than the lead core M80 projectile. Aluminum targets which can be penetrated by both rounds at muzzle velocity range from 1/2 inch at 60 degrees obliquity to 1.25 inch at normal impact. At the thicker normal targets, the M59 requires about 250 fps less to penetrate, and at the thinner oblique targets, about 50 fps less is required by the M59 over the M80. This phenomenon against aluminum targets is that the aluminum is hard enough to deform the lead core of the M80 such that it expands to a larger diameter, adding further resistance to penetration. The steel core of the M59, however, will not deform significantly, so it remains more streamlined as it penetrates. This accounts for the greater efficiency of the steel core at normal impact against aluminum. This effect is lost to a degree against oblique aluminum targets, since the more streamlined steel core will begin to deviate in the aluminum target and its trajectory will be slightly longer before it breaks out of the back surface. Against very thick aluminum targets at high obliquity, non-deforming bullet cores have been known to broach. That is, their penetration trajectory curves to the point where the core actually exits from the impact surface, but at a considerable distance from the entrance point. The lead core is not susceptible to changing direction while penetrating aluminum, since it remains stable due to its continued deformation. In any event, for this caliber ammunition, the steel core M59 retains a slight edge over the lead core M80 against aluminum targets at all obliquities.

Neither of these rounds, however, is considered an armor piercing bullet. This comparison was made only to see if substituting a mild steel core for the currently employed lead-antimony core would present a performance risk against this target set. This data indicates that on the average, no performance degradation occurs when using the steel core, as in the M59 design, and in some cases performance slightly improves.

(b) Plastic and Composite Target Performance Comparisons

Ballistic test data exists, and is online in the SAA AADS data base, for both the M59 and M80 rounds against fiber glass (WRF) (Figures 6a,b,c), typically used for

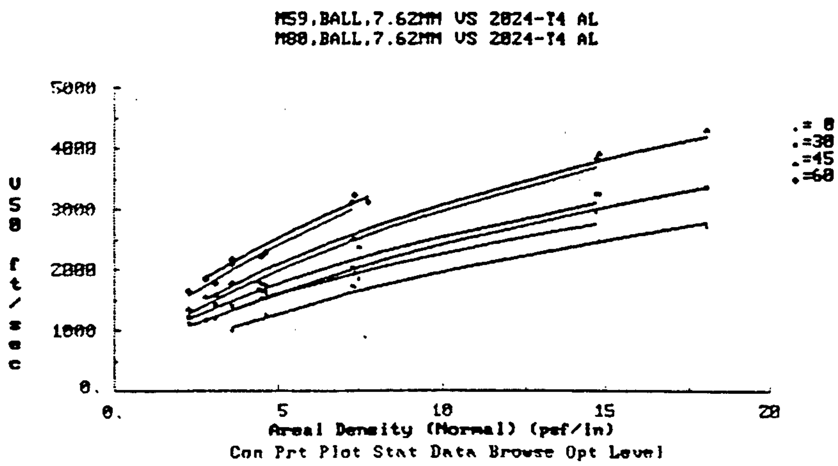


Figure 5(a)

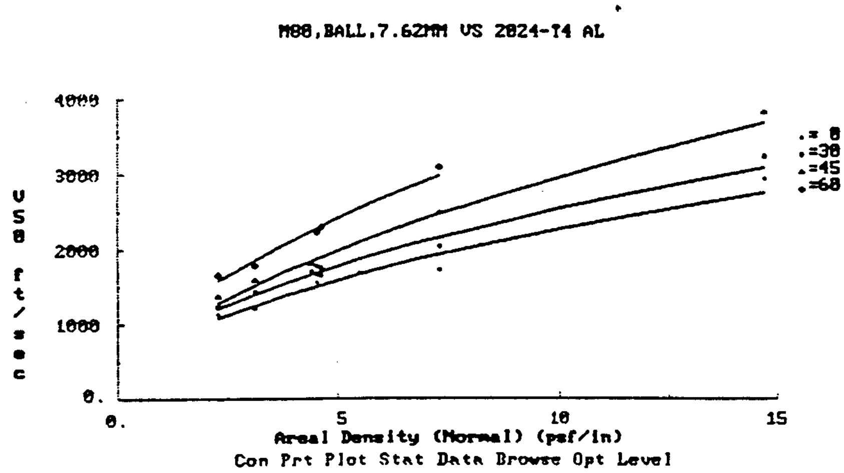


Figure 5(b)

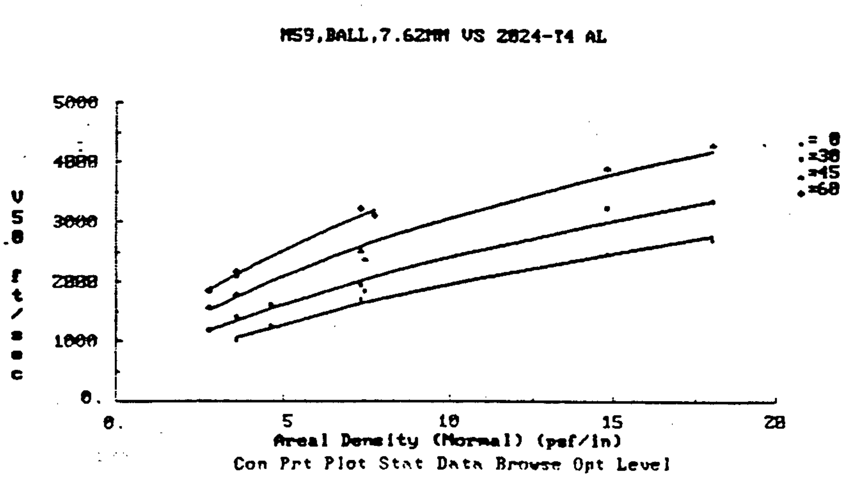


Figure 5(c)

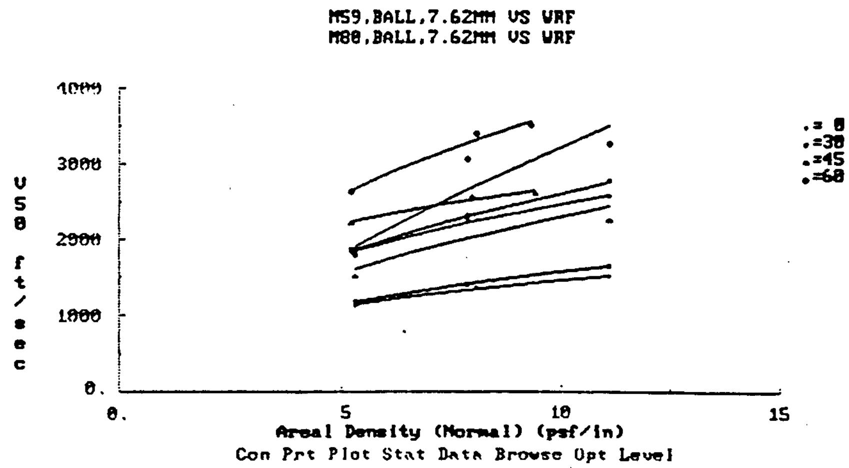


Figure 6(a)

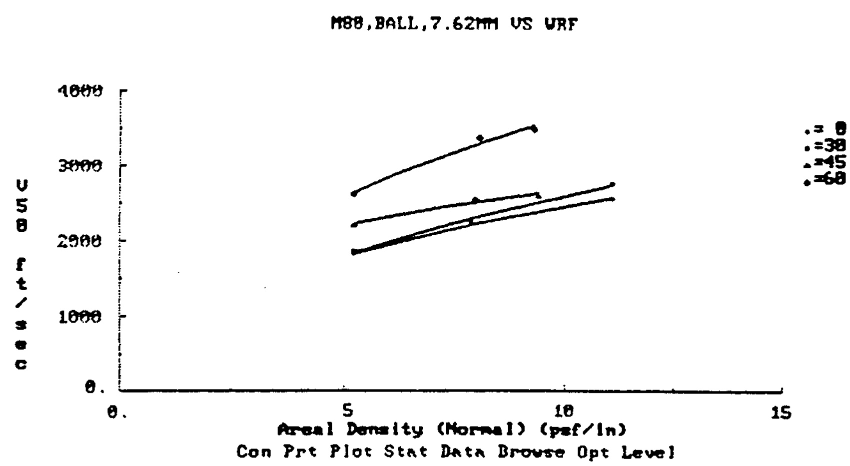


Figure 6(b)

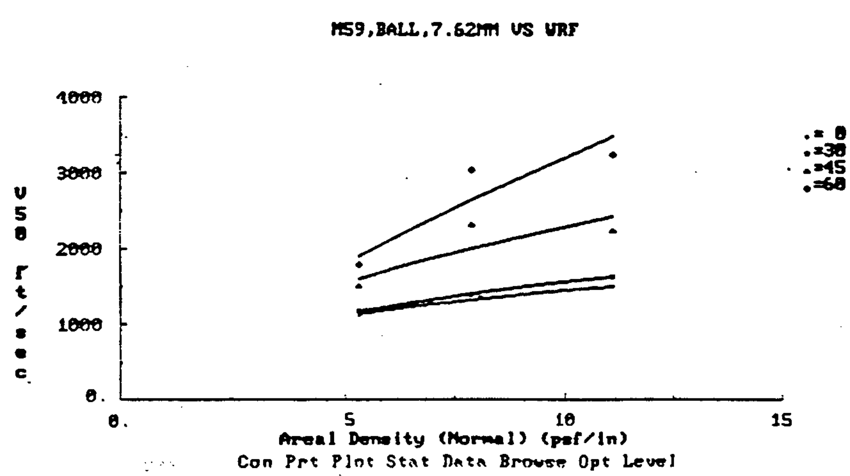


Figure 6(c)

protection in light vehicles and shelters, and Kevlar composite laminates (Figures 7a,b,c), typically used for helmets and other body armor. These two materials are considered to be relatively soft targets, and as one would expect, the steel core M59 performs better than the lead core M80. These effects are similar to that of the aluminum target, which is capable of deforming the lead core, but not the steel core. The M59 requires about as much as 1000 fps less velocity than the M80 against WRF depending on obliquity, and as much as 500 fps less velocity than the M80 against thick vertical Kevlar targets. Against thinner oblique Kevlar, the difference in performance is not as great. Again, it appears that the use of steel in the bullet core of ball rounds does not degrade overall performance as compared to a similar lead core bullet.

5. Design and Ballistic Match of Toxic-Free 7.62mm Ammunition

(a) Lead Substitutes

The M59 steel core bullet still retains 39 grains of lead-antimony alloy filler. The amount of lead in the M59 is approximately 35% of that in the M80. This demonstrates that at least this amount of lead can be replaced by steel without degrading performance, however, the M59 is still unsuitable as a truly toxic-free bullet. Both rounds are ballistically matched, in that they have effectively the same weight, form factor, ballistic coefficient, and muzzle velocity. Therefore, they will fly the same trajectory.

Given the requirement under this task to ballistically match to this family of ammunition, one course of action is to take these designs and substitute another, non-toxic, material for the lead. Three materials appear as candidates from our material and toxicity investigations -- bismuth, copper, and molybdenum. Bismuth has 86%, copper has 78%, and molybdenum has 90% of lead's density. Substituting one of these metals for the lead contained in either the M59 or M80 would yield a straightforward solution. The resulting projectile will almost certainly have to be slightly different from these existing rounds, but we do not see any difficulty making adjustments in form factor or dimensions to keep the resulting ballistic coefficient

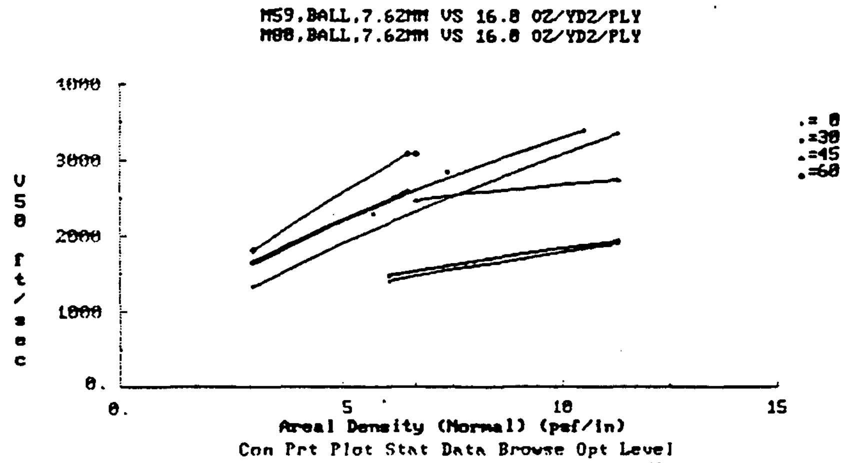


Figure 7(a)

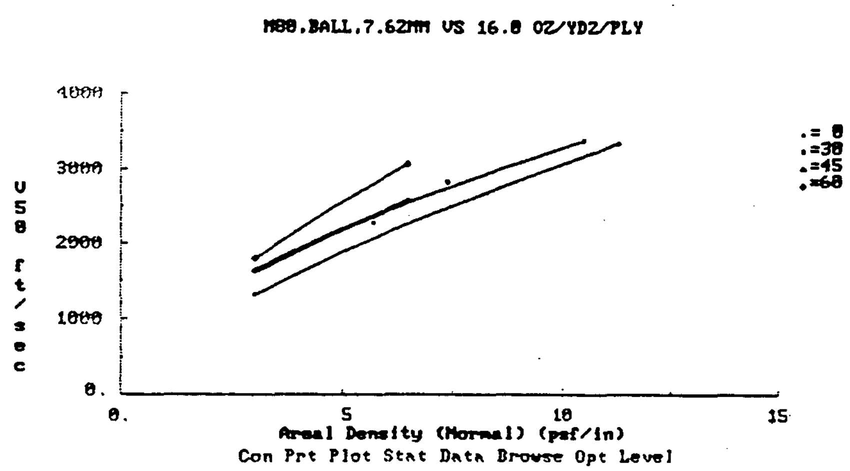


Figure 7(b)

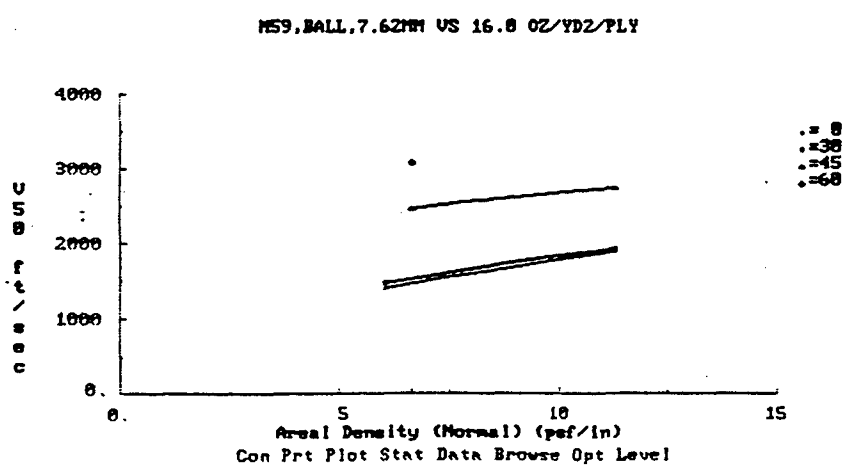


Figure 7(c)

equivalent.

An M80 substitution using bismuth or molybdenum would be slightly longer than the current M80 to achieve equivalent weight (150 grains), but not as long as the M59. Therefore, the bullet form factor should not change. However, the gyroscopic stability factor decreases by using the less dense material in a longer bullet, but an adequate margin remains even to -40 degrees centigrade. Ironically, lengthening the M80 design to accommodate a pure copper core with a 150 grain weight results in a pure copper core M59 design. In other words, remove all the lead and steel from the M59 and put copper in the existing copper jacket, and the bullet weighs 150 grains. The gyroscopic stability factor does suffer, however, with a pure copper M59. The stability margin is adequate at service temperatures, but at -40 degrees C the bullet is at the margins of stability. The resulting bullet form may have to be slightly different to regain some stability margin safety factor, but we do not see any difficulty making adjustments and keeping all relevant trajectory parameters within tolerances.

Substituting bismuth or molybdenum for the lead contained in the M59 would also yield a straightforward solution. A one-for-one substitution bismuth based M59 would weigh 146 grains and a molybdenum based M59 would weigh 147 grains. Since the original bullets weigh approximately 150 grains, there would be negligible difference in the trajectory parameters. In any event, the bullet could be slightly lengthened to make up the difference in weight. The M59 design can still be stretched and retain good gyroscopic stability, with bismuth or molybdenum as a lead substitute, and still retaining the steel core. Close attention, however, will have to be paid to not introducing more drag due to the longer body and any resulting change in the yaw drag as the projectile precesses during flight. In either case, an aerodynamically successful design is certainly within the realm of feasibility.

The substitution of copper for the lead in the M59, while retaining the steel core, is not feasible, due to loss of gyroscopic stability. Since the steel core has less inertia than an equal volume copper core, the only alternative for the use of copper is in the form of a pure copper based bullet. As previously discussed, such a bullet will, in fact, have the form of the M59.

Candidate solutions presented thus far include a copper jacketed bullet with either a pure copper (jacket not necessary), bismuth, or molybdenum core in the M80 configuration, or an M59-type steel core bullet with bismuth or molybdenum as a lead substitute. Since the lead in the M59 design was shown to provide negligible terminal ballistic performance, and that it is the steel core that actually defeats the target, the use of bismuth or molybdenum should not affect the penetration characteristics of such a bullet design. Bullets using pure copper, bismuth, or molybdenum cores may, however, have different terminal ballistic performance than a pure lead core bullet.

This issue of differences in terminal ballistic performance of pure copper, bismuth, and molybdenum will require further study. Although the mass of these substitute bullet cores may be designed to be equal to the mass of the original lead core but with more volume, it is important that the non-lead cores deform similarly to the lead against candidate targets. In this manner, the kinetic energy of the cores will be properly deposited on the target. Bismuth is the closest to lead in physical properties such as hardness and melting point, which will affect its softening and ductility upon impact with a target. It will most likely perform similarly to lead.

Copper and molybdenum, however, have significantly higher melting points and hardness than lead. Relatively speaking, copper is significantly harder and stronger than lead, and molybdenum even more so. They will most likely resist flattening out against a steel or composite targets and respond significantly different than lead. In the case of copper and molybdenum cored bullets, it may be better to choose properties which begin to mimic those of the mild steel core in the M59 bullet. In this manner, target penetration performance will be preserved. A suitable copper cored bullet may in fact perform better in the form of brass or bronze, which is available in many forms with greater strength and hardness than pure copper. The use of pure molybdenum in its hardest condition may result in an armor penetrating bullet. Manufacturing processes to reduce its hardness and strength will have to be investigated. Nevertheless, adequate solutions to the use of copper and molybdenum based bullet cores is a possibility.

The decision to use either bismuth or molybdenum as a lead substitute raises two additional non-trivial issues. The first issue is the long term cost and supply of the material. As mentioned earlier, it is unclear to what extent even a small change in the material demand will affect global price and availability. In addition, both these materials are mined as by-products of another ore: bismuth from lead mining, and molybdenum from copper mining. It is unlikely that Army bismuth or molybdenum demands could reverse this product-by-product relationship, or that one would want to. One might question the policy of promoting lead mining to increase the supply of bismuth. Therefore, as world demand for lead and copper fluctuate or decline, the availability of these lead substitutes will vary as will their price.

The second issue with the use of bismuth and molybdenum involves their toxicity. Although current standards and available information rate them as low risk, one ultimately does not know their toxicity until they are proliferated and are involved in many uses. For many years, lead was considered safe for many applications. Only recently has it and many other commonly used materials been ruled dangerous. Therefore, there is a risk that both bismuth and molybdenum will be discovered to have some toxic qualities, yet undetermined.

(b) An All Steel Core Projectile

Considering these issues, a second alternative to getting the lead out of the ball round is to take the M59 concept and go all the way with eliminating the lead filler by using a full steel or iron core. Iron or steel is a good candidate from both a toxicity and cost perspective. Steel is one of the few metals that is cost competitive with lead. The toxicity of iron is well understood, it is of low risk, and the material has been in use for millennia. An iron based core will also simply rust away without the need for cleanup, or cleanup can be accomplished with a magnet. The target penetration performance of steel core bullets is also acceptable compared to lead core bullets. For ball ammunition applications, an iron filler would also perform adequately.

However, as previously discussed, one cannot simply make a direct material substitute in the M59 and retain exact ballistic similitude. This approach, therefore, raises another issue, which is how close a ballistic match is sufficient, for both training and service use of the cartridge. Typical requirements in other small calibers, 5.56mm for example, are for a ballistic match of 1 mil. This translates to 1 foot deviation at

1000 feet, or 1 yard at 1000 yards. A 1 mil ballistic match is most probably sufficient for U.S. Army 7.62mm general purpose ammunition requirements, since currently fielded 7.62mm systems are machineguns and miniguns, which are intended as suppression weapons and not for marksmanship. Marksman and snipers also generally rely on specially loaded match grade ammunition, and in any event, they certainly re-zero their weapon when switching from different ammunition lots and types. A NATO STANAG for this cartridge may require a tighter match, since by agreement our allies should be able to use any 7.62mm x 51mm available, and many of our European allies issue 7.62 mm rifles within the ranks. For general service issue, however, we believe we can design an all steel core cartridge with better than 1 mil ballistic similitude.

Beginning with the basic M59 shape and substituting steel for the remaining lead filler results in a bullet weighing 139 grains, or approximately 92% of the M59. This gives a slightly lower ballistic coefficient and one would expect this round to lose velocity faster and demonstrate more trajectory height at long range. At service muzzle velocity, this round will ballistically match the M59 within 9 inches out to a range of 2300 feet. This corresponds to a match of at least .33 mils. As target range decreases this match, of course, gets better. At 1000 feet the match is .04 mils. Since this round is lighter than the M59/M80 series, it is also possible to adjust the propellant load to increase the muzzle velocity, within safe pressure limits. Increasing the muzzle velocity will result in the bullet flying slightly above the current trajectory early, but not dropping as far at greater ranges. A 50 fps muzzle velocity increase gives a ballistic match out to 2400 feet of less than 1.4 inches or .07 mils.

This ballistic match would be considered extremely good by any standard. The only drawback to filling the M59 projectile entirely with steel is that the stability parameters change dramatically. The gyroscopic stability factor is significantly reduced by using the less dense steel filler in the tip and tail region of the projectile. The steel filled bullet has a gyroscopic stability factor of only 1.3 at 59 degrees F at service velocity. At -40 degrees F the bullet is just barely gyroscopically stable. Therefore, there is a risk at cold temperature that the bullet will tumble in flight, and be sensitive to traditional ballistic disturbances, such as reverse flow at the muzzle exit. Some experimentation would have to be performed to determine these performance parameters.

Substituting steel for the filler in the M80 design gives a bullet with acceptable stability parameters, due to its shorter length. Gyroscopic stability at muzzle velocity and 59 degrees F is approximately 1.7. This bullet, however, weighs only 115 grains or about 77% of the weight of the M80. Its trajectory parameters will suffer accordingly. At current service velocity, this round will only match to 1.3 mils at 2100 feet. This improves proportionally at shorter range, however. At 1200 feet, match is within .33 mils. Adding 150 fps to the muzzle velocity improves the match of this round to a maximum error of .52 mils at 2300 feet. At 1200 feet range, this match improves to .12 mils.

Most likely, the best solution is somewhere in between an all steel core M59 and M80, in terms of bullet length, weight, and stability, along with a slight increase in muzzle velocity to compensate for the lighter bullet weight compared to the current service rounds. This approach is certainly within the region of feasibility.

Section 8

Recommendations

The objective of a program to eliminate toxic materials can take two independent directions. First, we can think in terms of cleaning the range after firing. This may necessitate frequent cleaning in order to ensure that toxic effluents do not runoff into ground water. The second option is to design service and/or training cartridges that are non-toxic to an acceptable degree. This appears to be feasible and is probably preferable.

In accordance with these guidelines, our recommendations are as follows:

1. It is first necessary to formulate a formal ARDEC position, including a document and presentation material. This material should be self-contained and should address the requirements of the Army Environmental Program. It should describe the objectives of the design effort, how the design effort will integrate into the DA infrastructure, and how documentation will be generated to support the Army objectives in this area.

In addition, the important logistics considerations should be addressed as part of this ARDEC position. All ammunition designed under this effort will be ballistically similar to current ammunition, and relevant performance parameters will not be compromised. The manufacturing considerations are important, and it is necessary to discuss that the new cartridges can be made on existing facilities, and that costs will be consistent with constraints. Finally, the issues related to materials are important, and if a new metal is to be substituted for lead, do we have an adequate supply, and will the additional requirements impact availability or price?

2. The simplest modification is to simply substitute bismuth and/or molybdenum for the lead, using the current M59 design as a baseline, with no jacket modifications.

The weight of this modified round will be about 97% of that of the M59. Any trajectory variation should be minimal, and this can be calculated and the final trajectory modified by minor shape iterations, if necessary. Terminal ballistics should remain the same as for the M59. Assess cost impacts on materials and manufacturing. A quantity of this round can then be tested for type classification.

3. The next level of design complexity is to develop a copper-based M59 derivative projectile (approximately 150 grains) in either pure copper (jacket material), or copper jacketed brass or bronze as terminal ballistics require. A slight redesign will be necessary in order to ensure adequate cold temperature stability margin and minimal sensitivity to transient muzzle and trajectory conditions. Test trajectory and terminal ballistics. Assess cost impacts on materials and manufacturing.

4. The highest payoff is to develop a copper jacketed all steel core bullet, which has adequate stability margins at service and cold temperature, but compromises on bullet weight. Initial ballistic calculations indicate that a 125 grain bullet with length greater than M80, but less than M59 will work well. Trajectory drop will be compensated for with greater muzzle velocity, achievable with the lower projectile weight. This round will have equivalent, and perhaps enhanced, lethality and low life-cycle cost, due to the elimination of cleanup requirements. Test trajectory and terminal ballistics and assess cost impacts on materials and manufacturing.

Section 9

Conclusions

There are several important conclusions that can be made from the research that was performed in response to this task order.

1. The various legislative and legal issues that have been put in place to address the issues of toxicity and DA procedures and policy are contradictory and appear to be inadequate. The responsibilities and obligations of DA are not clear. The roles of other executive and legislative agencies (such as EPA and HHS), with respect to DA, are not clearly defined.

2. The issues of "lead-free" and "toxic-free" are frequently taken to be identical. There is no doubt that lead, in certain forms, has serious toxic effects. However, many of the alternatives that have been, and are now being, seriously considered as substitutes are potentially even more toxic as well as more difficult to remove from the environment. To a large degree - most heavy metals can be considered to be toxic to some degree.

3. Although several organizations are currently either working on toxic-free ammunition, including non-toxic primers, or have products available; there is no definitive technology available that is ready for immediate deployment.

4. Lead is a material of choice for ball ammuntiion due to its high density and low cost. Analysis indicates that other materials and technologies can result in equivalent performance. Since life-cycle costs are important, steel is one material that immediately suggests itself as the most likely candidate to substitute for lead.

Appendix I

Toxicity of Tungsten

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Bibliography

Summary from Danesi Report

APPENDIX C

TOXICITY OF TUNGSTEN

This Appendix reviews studies reported in the literature on the toxicity of tungsten.

Abstract

Tungsten toxicity, as measured by oral LD_{50}, is greatest for soluble tungsten compounds, but varies according to species. The oral LD_{50} for mice exposed to sodium phosphotungstate is 240 ± 13.5 mg/kg while rats have an oral LD_{50} of 1,190 ± 129.5 mg/kg. Sodium tungstate has an oral LD_{50} of 875 mg/kg in rabbits.

Dose-related declines in food intake and decreased weight-gain have been reported in rats receiving dietary tungsten exposure with the greatest of these effects observed in females. Sodium tungstate fed to rats lowers blood cholinesterase while rabbits, similarly treated, show decreased sulfhydryl concentrations in blood and serum; blood glucose levels are 20-25% higher than controls in tungsten fed rabbits one hour after intravenous galactose loading[1].

Inhalation and intratracheal exposure of tungsten to animals usually produces lung irritation similar to that produced by "inert" dust. However, different inhalation experiments utilizing soluble tungsten compounds have demonstrated a variety of lung-tissue component responses. Rats exposed to

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[1]The reports of tungsten interference with cholinesterase levels in the blood, and presumably throughout the system of exposed animals coupled with the reported symptomology of tunsten workers (see this review) suggest that tungsten may be responsible for acetylcholine accumulation as is observed in organophosphate poisoning. Accumulation of acetylcholine is believed to be responsible for the tension, anxiety, restlessness, headache, insomnia, neurosis, emotional instability, apathy, tremor, ataxia, convulsions, and depression of respiratory and circulatory centers. The reports of tungsten actions on ictal activity and glutaminase further suggest a neurological bias in tunsten health effects.

tungsten silicide by inhalation and by intratracheal administration for 6 months developed hyperplasia of the lymph nodes, increased collagen in the lungs, and sporadic thickening of the alveolar walls.

C.1 PHARMACOKINETICS

C.1.1 Inhalation Exposure And Distribution

Inhalation studies with ^{181}W-tungstic oxide in beagle dogs were reported by Aamodt (1975). Following inhalation, 60% of the inhaled activity was deposited in the respiratory tract. Of this about one-half was located in the lower portion of the tracheobronchial compartment and in the pulmonary compartment. Blood measurements indicated that inhaled tungstic acid entered the blood soon after inhalation and was removed rapidly. Measurements of selected organ and tissue samples at sacrifice (165 days post-inhalation) showed the highest test concentration of tungsten to be in lungs and kidney. Bone, gall bladder, liver, and spleen were reservoirs of tungsten by a factor of 10 less than the lung while the tungsten activity in the remaining organs decreased in the order, testes, pancreas, large intestine, small intestine, diaphragm, stomach, heart, and skeletal muscle. In terms of total organ burdens most of the tungsten actively was found in bone (37%), lung (31%), kidney (15%), liver (9.7%), and skeletal muscle (5.7%).

C.1.2 Oral Exposure And Distribution

Oral administration of ^{181}W labeled sodium tungstate to rats resulted in the greatest concentration of tungsten to be found in the spleen followed, in descending order of concentration, by kidney, pelt, bone, and liver. (Ballou 1960). Kaye (1968) who orally administered ammonium tungstate and sodium tungstate in KOH to rats reported the concentration of tungsten in the bone to be ten times that of the spleen which contained the next greatest activity. Other organs with significant tungsten concentrations in this study, in order to decreasing concentrations were hair, kidney, pelt, and liver. Twenty-four hours following administration of sodium tungstate by gastric intubation in rats

Fleischman, et al. (1966) found the highest concentrations of tungsten was found in kidney followed by bone, spleen, and seminal vesicles.

Kinard and Aull (1945) described the distribution of tungsten in rat tissues after dietary feeding of tungsten and its compounds (tungstic oxide and sodium tungstate equivalent to 0.1% tungsten, ammonium-p-tungstate equivalent to 0.5% tungsten, tungsten metal at 2 and 10% tungsten) during a 100 day experimental period. This investigation indicated that bone and spleen were the major sites of tungsten deposition. The concentrations ranged from 8 to 18 mg % in bone and from 2 to 14 mg % in the spleen with averages of 11.5 and 7.5 mg %, respectively. Only traces of tungsten (less than 1 mg %) were present in the skin, kidney, and liver. The blood, lungs, testes, and muscles showed traces of tungsten only in some cases. Except for a single instance for each organ, the brain heart and uterus were free of tungsten. The investigators concluded that there were no marked differences among the distribution patterns of the various tungsten compounds tested. However, since the doses of tungsten administered as various tungsten compounds were not comparable, this conclusion may not be valid.

C.1.3 Exposure By Injection And Distribution

Scott (1952) reported the greatest concentration of activity in the kidney one-day after intravenous injection of ^{181}W-sodium tungstate in rats. Other tungsten retaining tissue, in order of descending tungsten concentrations, were liver, spleen, and small intestine. Bone showed little activity. However, Fleishman et al. (1966) found that bone showed the highest tungsten concentration 24 hours following intraperitoneal injection of ^{181}W-sodium tungstate in rats. In the experimental results reported by Fleishman et al. (1966) kidney, seminal vesicle, and spleen followed bone in order of descending concentrations of tungsten retained.

C.1.4 Biological Half-Time

In the study by Kaye (1968), elimination of gastrically administered tungsten from the rat was very rapid, with a biological half-time of about 10 hours for the initial fast component of the elimination curve. Elimination of tungsten from soft tissues was relatively rapid, but a biological half-time of 44 days was observed for the spleen. The biological half-time for ^{185}W in bone was calculated to be 1100 days for the slowest component of a three-day component elimination curve.

In Aamodt's experiments (1973, 1975) 82% of injected ^{181}W-sodium tungstate was removed rats with a biological half-time of 86 minutes, 15% with a half-time of 8.8 hours, 2% with a half-time of 3.65 days, and 1% with a 99-day half-time. Inhaled ^{181}W-tungstic oxide in dogs was removed with a biological half-time of a little less than 9 hours for 94% of the activity in the visceral area, with the longest half-time of 139 days for 1.6% of the activity. In the partial body measurements made over the lung area, about 69% of the activity was lost with a biologic half-life ($t_{1/2}$) of 4 hours, the next 23% with a $t_{1/2}$ of 20 hours, 4.6% with a $t_{1/2}$ of 6.3 days, and 3% with $t_{1/2}$ of 100 days.

C.1.5 Excretion

All reports reviewed (Scott 1952, Ballou 1960, Fleishman et al. 1966, Kaye 1968, Aadmodt 1973, 1975) agree that much of the absorbed tungsten is rapidly excreted in the urine. Kaye (1968) found that 40% of the administered dose of ^{181}W was excreted by the kidney in the first 24 hours, but very little was excreted in the urine thereafter. An additional 40% of the administered dose recovered from the feces in the first 24 hours is likely to have been largely unabsorbed tungsten together with tungsten removed in the gut with intestinal secretions and bile. By the end of 3 days, fecal elimination had accounted for 52% of the administered does.

Following intravenous administration of ^{181}W-sodium tungstate in beagle dogs, 91% of the injected activity was excreted in the urine within 24 hours (Aamodt 1973). The ratio of activity excreted in the urine to that eliminated in the feces averaged 38. While loss from the blood during the first 24 hours was very rapid, it was calculated that some of the tungsten, perhaps that bound to red blood cells or to plasma proteins, was not filtered from the plasma, or was being reabsorbed from the glomerular filtrate. The rate of decrease in blood activity following inhalation of tungstic oxide aerosol was lower than for injected sodium tungstate, but this could be accounted for by activity entering the blood from the lung and the gut over an extended period of exposure (Aamodt 1975). The ratio of cumulative urinary excretion to cumulative fecal elimination for 165 days ranged from 0.57 to 1.8, the variation being related to differences in clearance patterns of individual dogs.

In man, trace quantities of tungsten are excreted in urine and feces. In a limited study on four normal young adults without specific exposure, the elimination of tungsten by urine and feces over 24 hour periods balanced the tungsten intake in food. The urinary excretion ranged from 2.0 to 13.0 ug tungsten per 24 hours in these four subjects in 8 estimations, fecal elimination ranged from 1.6 to 5.7 ug tungsten per 24 hours (Wester 1974).

C.2 TOXICOLOGY

C.2.1 Neurotoxicology

Sodium tungstate administered to rats at doses of 0.05 and 0.5 mg/kg caused pronounced disturbances in conditioned reflexes (Nadeenko 1966). The latent periods of sodium tungstate-treated animals were 1.6 - 1.7 seconds for bell stimulus and 2.4 - 2.7 seconds for light stimulus, compared to 0.9 and 2.0 seconds, respectively for controls. Animals given the maximum doses of sodium tungstate exhibited a larger number of extinctions of the conditional reflexes. Disturbances of conditioned reflexes were indicated by a statistically significant increase in the number of equalizing and paradoxical phase states. Nadeenko (1966) noted that the study of extinction and recovery of a conditioned response to a bell revealed a pronounced decrease in the lability of nervous processes in the cerebral cortices of 0.05 and 0.5 mg/kg dose groups. Necrotic lesions and destruction of the apical portions of the intestinal villi were also evident in these animals. Nadeenko found that tissue accumulations of tungsten were dose-dependent with the highest dosages of tungsten received resulting in the greatest tissue concentrations of the metal. These findings correlated with the physiological measurements reported and led the investigator to conclude that tungsten has a cumulative toxicity.

Karantassis (1924) reported that guinea pigs exposed to tungstate by gastric intubation developed uncoordinated movement, sudden jumps, trembling, and breathlessness. Humans exposed to tungsten dusts in occupational circumstances complained of increased headaches, dizziness, nausea, and impaired sense of smell (Vengerskaya and Salikhodzhaev 1962).

Tungstic acid is used to produce experimental epilepsy in laboratory animals (Kusske et al. 1974). The application of 0.02 ml of tungstic acid gel to the surface of a cat brain cortex gives rise to abnormal EEG activity after a 20-30 minute interval which increases and results in sustained ictal activity. The effect produced is so consistent that it has been used to produce model systems of experimental epilepsy.

C.2.2 Oral Toxicology

Kinard and Van de Erve (1940) evaluated the comparative oral toxicities of tungstic oxide, sodium tungstate, and ammonium-p-tungstate in male and female rats. Rats had 100% mortality when fed diets containing ammonium-p-tungstate equivalent to 5% tungsten, tungstic oxide equivalent to 3.96% tungsten and sodium tungstate equivalent to 2% tungsten. Tungstic oxide given at a level equivalent to 0.5% tungsten caused 80 and 66 percent mortality in males and females respectively while sodium tungstate, at the same level, caused 50 and 66 percent mortalities in males and females, respectively. In comparison, 0.5% tungsten as ammonium-p-tungstate caused no death. Sodium tungstate and tungstic oxide caused no death in concentrations equivalent to 0.1% tungsten.

Oral toxicity studies for various compounds of tungsten measuring a variety of parameters with different compounds and selected species were reported in a 1966 study by Nadeenko. For sodium phosphotungstate, an LD_{50} of 240 $\pm$ 13.5 mg/kg for mice and an LD_{50} of 1,190 $\pm$ 129.5 mg/kg for rats was determined. Similar studies were reported for tungstic oxide, but the conclusions are not clear, possibly because of problems in translating the Russian text. Nadeenko (1966) does conclude that tungstic oxide is less toxic than sodium tungstate and sodium phosphotungstate because of its lower solubility. In a separate series of these experiments Nadeenko (1966) determined the sodium tungstate oral LD_{50} for rabbits and guinea pigs to be 875 mg/kg and 1,152 mg/kg respectively.

Nadeenko (1966) also studied the effect of (presumably daily) oral doses of sodium tungstate (10, 25, 50, and 100 mg/kg) on physiologic functions and systems in rats and rabbits. All doses produced growth retardation and lowered blood cholinesterase activity in rats: in rabbits the sulfhydryl concentrations of whole blood and serum were decreased and synthesis of glycogen in the liver was disturbed. Stained sections of the gastrointestinal tract and kidneys showed signs of increased vascular permeability, hemorrhages, degenerative dystrophic changes, and moderate proliferative cellular reaction. No distinction in these biological effects was indicated with respect to sex. During the chronic phase of these studies, rabbits receiving sodium tungstate doses of 5.0 and 0.5 mg/kg had concentrations of blood glucose at levels of 20-25% higher than controls one hour after intravenous galactose loading.

Kinard and Van de Erve (1940) noted dose-related declines in food intake accompanied by decreased weight gain in dietary tungsten studies. The greatest decrease in weight gain noted in these experiments was for female rats.

C.2.3 Pulmonary Toxicology

In both short- and long- term animal experiments, the major effects of inhalation or intratracheal exposure to tungsten and its compounds have been reported as limited to the respiratory system. Menzentseva (1967) reported that lungs of rats exposed by inhalation to tungsten carbide at 600 mg/m^3, 1 hour/day, for 5 months showed proliferative reactions to the lymphoid histiocytic elements and uniform thickening of the alveolar walls followed by mild fibrosis. Mezentseva (1967) also reported that rats given single intratracheal doses of 50mg of either metallic tungsten, tungsten carbide, or tungsten trioxide showed no severe pulmonary changes under microscopic examination.

Delahant (1955) reported that neither metallic tungsten nor tungsten carbide given intratracheally to guinea pigs irritated lung tissue. Similarly, Miller et al. (1953) observed mobilization of septal cells; engulfment of pigment; and accumulation of air sacs, lymphoid tissue and alveolar walls in rats given 10% suspensions of tungsten intratracheally in a manner typical of those effects produced by inert dust.

However, Schepers (1955) found that intratracheal injection of tungsten carbide and carbon in weekly doses of 50 mg of a (94:6) mixture caused acute hyperemia and bronchial inflammation in guinea pigs. Minor residual changes such as the development of subpleural fibrocellular granulomata, were also noted in the lungs. Brakhnova and Samsonov (1970) reported that inhalation and intratracheal exposure of rats to tungsten silicide of 1-6 months caused hyperplasia of the lymph nodes, sporadic thickening of the alveolar walls, and increased collagen in the lungs. There results suggest that tungsten and some of its compounds, such as those most frequently encountered in the cemented tungsten carbide industry, have distinctive toxicities.

C.3 BIOCHEMICAL TOXICOLOGY

C.3.1 Potential Teratogenic Effect

Tungsten is the element most chemically similar to molybdenum and is the only substance known that is capable of producing experimental molybdenum deficiency in animals. This is accomplished by tungsten's ability to replace molybdenum in sulfite oxidase and to prevent the incorporation of molybdenum into xanthine oxidase. In the case of xanthine oxidase, inactive apoprotein is synthesized when WO_4^{-2} is fed (Johnson et al. 1974), but in the case of sulfite oxidase up to 35% of the molybdenum-free enzyme contains tungsten. (Cohen et al. 1974). Cardin and Mason (1976) concluded from their studies on the gastrointestinal absorption and transport of molybdate are sufficiently non-specific to accept tungsten over molybdenum.

In humans, genetic deficiency of xanthine oxidase appears to be relatively harmless (Watts et al. 1964). Therefore the ability of tungsten to interfere with the activity of this enzyme by preventing the incorporation of molybdenum has not been shown to constitute a serious toxicological condition.

However, in the case of sulfite oxidase, the potential for serious complications arising from tungsten exposure in such a way as to affect sulfite oxidase has been observed (Cohen et al. 1974). A fatal case of sulfite oxidase deficiency has been reported in a human patient (Irrevere 1967). The patient was born with neurological abnormalities and deteriorated to a virtual decorticate state by 9 months. Bilateral ectopia lentis was discovered at 1 year. The patient was studied at the age of 30 months. Urine was found to contain abnormally increased amounts of S-sulfo-L-cysteine, sulfite, and thiosulfate. Urinary excretion of inorganic sulfate was markedly reduced and did not increase after administration of L-cysteine. These chemical abnormalities were best explained by the presence of a block to conversion of sulfite to sulfate. Studies from tissues obtained from the patient is post-mortem revealed a marked deficiency in sulfite oxidase.

Cohen et al. (1974) reported that the development of both sulfite oxidase and xanthine oxidase is very much impaired by the administration of tungsten to pregnant rats 20 days before birth of the litter. Creation of simultaneous deficiencies of sulfite oxidase and xanthine oxidase in adult rats by administration of tungsten has no observed deleterious effects on these animals, but does render them highly susceptible to toxicity from bisulfite and SO_2 (Johnson et al. 1974). Apparently, normal development of sulfite oxidase leads to the accumulation of inactive molecules in the livers of offspring of tungsten fed rats. Development of succinate cytochrome c-reductase and adenylate kinase is not affected by tungsten treatment.

C.3.2 Direct Enzyme Action

Sodium tungstate has been shown to activate brain glutaminase increasing ammonia release, in contrast to ammonium molybdate which inhibits it. (Johnson et al. 1974). The tungsten activation is believed due to either elevation of phosphorus ion concentration in the brain or to activation of glutaminase by direct action on the molecule (Bech 1974).

C.4 CARCINOGENESIS (POTENTIAL)

Studies utilizing molybdate, tungstate, and vanadate have revealed that these agents block the transformation of cytosol-steroid complexes to their activated form (no effects of these compounds have been reported on an activated steroid receptor). Because these agents are potent phosphatase inhibitors it has been suggested that the process of steroid receptor activation involves a dephosphorylation of the receptor protein itself or of a regulatory component. Recent studies have indicated that sodium molybdate not only blocks the activation of the steroid receptor complex, but also blocks the DNA and nuclear binding capacity of activated rat liver glucocorticoid-reception complex. In a subsequent study tungstate was found to be able to extract the DNA-cellulose bound glucocorticoid-receptor complex at even lower concentrations than those shown to block binding-capacity by molybdate (Murakami et al. 1982). The significance of these enzyme-metal interactions may be important with respect to the development of lymphosarcoma. One of the critical actions of the glucocorticoid hormones is their ability to arrest the development certain tumors of lymphatic origin. In vitro, glucocorticoids inhibit the growth of lymphosarcoma cells and mouse fibroblast. Specific glucocorticoid binding protein present in the cytoplasm and nuclei of steroid-sensitive cells are reduced in amount in resistant cell lines (Goldstein, Arnow, and Kalmar 1974). Thus, in conditions favoring the initiation of lymphatic tumor growth, exposure to sufficient tungstate may be capable of overwhelming the glucocorticoid actions which inhibit this neoplasia via mechanisms described above in the interactions with the cytosol-steroid complexes and/or the DNA and nuclear binding capacity of the activated glucocorticoid reception complex.

C.5. CHEMICALLY INDUCED ESOPHAGEAL AND FORESTOMACH CARCINOGENESIS

Tungsten has been observed to reverse other cancer-inhibiting reactions.

In chemically-induced carcinogenesis studies, tungsten added to the drinking water (200 ppm) of male rats countered the inhibitory effect of molybdenum on NSEE-induced esophageal and forestomach carcinogenesis (Luo et al. 1983). Whether similar effects may also occur in humans remains to be investigated. Epidemiologic data indicate that breast cancer mortalities among the residents of tungsten-mining areas in China are markedly higher than the national average. However, no information on the tungsten intake from water and food in the tungsten-mining area, nor on the estrous cycle of women residing in high molybdenum-intake areas, is available at this time (Wei et al. 1985).

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Appendix II

Questionnaire:

Information Search of Toxic Free Ammunition

S. Adelman Associates
301 Maple Avenue West
Suite 100
Vienna, VA 22180
Phone: (703) 255-1536
FAX: (703) 369-2314

Questionnaire: Information Search of Toxic Free Ammunition

Company/Organization: ____________________
Point-of Contact: ____________________
Address: ____________________
____
Phone: ____________________

Questions: (Please use additional paper as necessary).

1. Do you manufacture, or plan to manufacture, cartridges up to .50 caliber that are expressly designed to be lead-free/toxic-free? Do you manufacture, or plan to manufacture, ammunition components such as primers, tracers, propellant, and/or bullets that may be used in such toxic-free cartridges?

2. Are these designed to be used only as training cartridges or components, or are they expected to be service cartridges, capable of taking the place of the current lead-based, with no significant degradation in performance?

3. What was the original purpose of the subject cartridges/components? Were they designed with the elimination of toxic materials as the prime purpose, or were they designed for another application and then adopted when the toxic-free requirement became significant?

4. What is your approach to the elimination of lead and/or other toxic materials from the bullet, or the neutralization of the toxic effects of these materials? (eg. use of non-toxic materials, encapsulation, etc.). What materials are used in the bullet? Please be specific, and include data sheets and other relevant material when available.

5. What specific technology, if any, do you apply to eliminate toxic effects from the primer, propellant and tracer? What materials and formulations are used? Do you supply these components to cartridge manufacturers?

6. Have you quantified any toxic effects of these cartridges or cartridge components, and what were the results? Do you have material safety data sheets on these formulations?

7. What is the development status of these rounds? (eg. available now as commercial products, developed and ready for manufacture, in development, in test). If they are not available now, when do you envision they will be available?

8. What calibers are these products available in, and what calibers could they be supplied in?

9. What is the performance or anticipated performance with respect to aging, storage, temperature, humidity, etc? Has this been validated by testing and/or field experience.

10. What will be the relative production costs, compared with the current cartridges or components, in equivalent production quantities? How were these costs arrived at?

Appendix III

Bibliographies

Information Search of Toxic Free Ammunition

VIII. REFERENCES

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IB81

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2/5/1 (Item 1 from file: 647)
03329488 DIALOG File 647: MAGAZINE ASAP *Use Format 9 for FULL TEXT*
Sharpshootin'. (big-game bullets, Rice Gun products) (column)
Seyfried, Ross
Guns & Ammo v28 p30(4) July, 1984
SOURCE FILE: MI File 47
ARTICLE TYPE: column
AVAILABILITY: FULL TEXT Online LINE COUNT: 00157
COMPANY NAME(S): Rice Gun Products Inc.--manufactures
DESCRIPTORS: Woodleigh Gunsmithing--manufactures; big game hunting--equipment and supplies; rifles--cleaning

2/5/2 (Item 1 from file: 6)
1634524 NTIS Accession Number: PB92-229145/XAB
Health Hazard Evaluation Report HETA-91-161-2225, Denver Police Department, Denver, Colorado
Lee, S. A. ; McCammon, C. S.
National Inst. for Occupational Safety and Health, Cincinnati, OH. Hazard Evaluations and Technical Assistance Branch.
Corp. Source Codes: 052678009
Report No.: HETA-91-161-2225
May 92 18p
Languages: English
Journal Announcement: GRAI9223
NTIS Prices: PC A03/MF A01
Country of Publication: United States
In response to a request from the Denver Police Department (SIC-9221) in Denver, Colorado, an investigation was made into lead (7439921) exposures during the use of different ammunition on the firing range. Ventilation rates were measured and personal breathing zone air samples were collected for ten officers during the firing of .45 caliber pistols. Nonlead primers were not yet available for .45 caliber ammunition. Air lead exposure ranged from 1.0 to 16 micrograms/cubic meter (microg/cu m). A slight improvement was noted in ventilation since an earlier NIOSH study had been performed at this site. The improvement resulted from the removal of a 3 foot high partition along the floor on the firing line. There was still, however, turbulent air flow across the entire firing line and backflow in some of the shooting booths. The author concludes that there was no health hazard from lead overexposure at this site at this time, but recommends use of jacketed bullets, nonlead primers, and administrative controls to minimize lead exposures.
Descriptors: *Occupational safety and health; *Environmental surveys; *Police; *Toxic substances; *Buildings; Toxicity; Occupational exposure; Lead poisoning; Air pollution effects(Humans); Ventilation; Ranges(Facilities); Ballistic ranges; Inhalation
Identifiers: SIC 9221; EPA region 8; Denver(Colorado); NTISHEWOSH
CAS Registry No.: 7439-92-1
Section Headings: 57U (Medicine and Biology--Public Health and Industrial Medicine); 57Y (Medicine and Biology--Toxicology); 89B (Building Industry Technology--Architectural Design and Environmental Engineering); 68G (Environmental Pollution and Control--Environmental Health and Safety); 68A (Environmental Pollution and Control--Air Pollution and Control)

2/5/3 (Item 2 from file: 6)
1113535 NTIS Accession Number: AD-B018 797/1/XAB
Reduction of Airborne Lead Contamination in Indoor Firing Ranges Using Modified Ammunition
(Final rept.)

Juhasz, A. A. ; Bowman, R. E. ; Samos, G.
Army Ballistic Research Lab., Aberdeen Proving Ground, MD.
Corp. Source Codes: 082505000; 050750
Report No.: BRL-1976
Apr 77 61p.
Languages: English
Journal Announcement: GRAI8510
Distribution limitation now removed.
NTIS Prices: PC A04/MF A01
Country of Publication: United States

PB 275 062/5

A study was conducted to evaluate the feasibility of decreasing or eliminating aerosol lead contamination hazards at indoor firing ranges by selectively modifying the ammunition fired. A caliber .38 Special police revolver was used in the study. Firings were conducted in a specially designed container which allowed trapping of particulate weapon effluents for subsequent analysis. Under the conditions of the experiment, conventional caliber .38 Special ammunition yielded an average of 5.64 milligrams of lead per round at the uprange position. Under identical conditions, custom-made ammunition, using copper jacketed soft point projectiles and a special lead free primer composition, yielded an average of 13 micrograms of lead per round. The data represented a decrease of lead contaminant produced per round by a factor greater than 400. The ballistic characteristics of the ammunition were also examined. There appears to be a good possibility of ballistically matching the modified ammunition with standard caliber .38 Special ammunition. (Author)

Descriptors: *Lead compounds; *Indoor air pollution; *Ranges(Facilities); *Firing tests(Ordnance); Revolvers; Police; Containers; Particulates; Ammunition propellants; Primers; Exterior ballistics; Projectiles; Ammunition components; Chemical analysis; Sampling; Muzzle velocity; Law enforcement officers
Identifiers: Cal. 38 ammunition; Cal. 38 guns; S/L change 8501; NTISDODXD
Section Headings: 13B (Mechanical, Industrial, Civil, and Marine Engineering--Civil Engineering); 68A (Environmental Pollution and Control--Air Pollution and Control)

1/5/1
00174429 DIALOG FILE 80 PTS ADM&T
POLLUTION FREE SHOOTING PRACTICE

International Defense Review 1985 v. 18 no. 8 p. 1357
ISSN: 0020-6512

Dynamit Nobel has developed Sintox, a non-toxic, lead-free zinc and titanium compound ammunition primer. In a parallel development, Dynamit Nobel has introduced Geco, a full metal case bullet. Both developments will reduce the heavy lead pollution at shooting ranges. Tests with Sintox over a 4-6 hr period produced a lead concentration of 0.007-0.0017 mg/m3 vs 9 mg/m3 over the same period using conventional Luger 9 mm ammunition. Dynamit Nobel has developed 9 mm and submachine gun rounds featuring the Sintox primer and Geco seal.

TRADE NAME: DETONATING PRIMERS; SMALL ARMS AMMUNITION; SINTOX; GECO

COMPANY: DYNAMIT NOBEL

PRODUCT: *Detonating Primers (2892141); Small Arms Ammunition (3482000)
EVENT: *Product Design & Development (33)
COUNTRY: *West Germany (4WGE)
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PAGE han,o,t,a;title=toxic 2 OF 3 RECORDS
06/06/85 [BOOKSM] [PTK] [MUMS] PAGE 1 OF 2
0*UPD* DISPLAYED RECORD HAS BEEN VERIFIED. 112
VERIFIED BOOK RECORD AACR 2

001 84-22755
050 RA1193.S58 1985
082 615.9/02 19
100 Sittig, Marshall.
245 Handbook of toxic and hazardous chemicals and carcinogens / by Marshall Sittig.
250 2nd ed.
260 Park Ridge, N.J., U.S.A. : Noyes Publications, c1985.
300 xxvi, 950 p. : ill. ; 25 cm.
500 Includes index.
504 Bibliography: p. 14-18.
020 ISBN 0-8155-1009-8 : $96.00
650 Poisons--Dictionaries.
650 Toxicology--Dictionaries.
650 Hazardous substances--Dictionaries.

PAGE han,o,t,a;title=toxic 3 OF 3 RECORDS
02/08/92 [BOOKSM] [PTK] [MUMS] PAGE 1 OF 2
0*UPD* DISPLAYED RECORD HAS BEEN VERIFIED. 112
VERIFIED BOOK RECORD AACR 2

001 91-16020
050 RA1193.S58 1991
082 615.9/02 20
100 Sittig, Marshall.
245 Handbook of toxic and hazardous chemicals and carcinogens / by Marshall Sittig.
250 3rd ed.
260 Park Ridge, N.J., U.S.A. : Noyes Publications, c1991.
300 2 v. (xl, 1685 p.) ; 26 cm.
504 Includes bibliographical references and index.
020 ISBN 0-8155-1286-4 : $197.00
650 Poisons--Dictionaries.
650 Toxicology--Dictionaries.
650 Hazardous substances--Dictionaries.
650 Carcinogens--Dictionaries.

PAGE t pattys;f=gb
NUMBER OF HITS=2 [FIND] [MUMS] SEQUENTIAL RECORDS 1 TO 2

1 Patty's Industrial hygiene and toxicology.
Theory and rationale of industrial hygiene practice / 1985
[GENBIB]
LC CALL NUMBER: RC967.T48 1985<SciRR> bi89-17345
2 Patty's industrial hygiene and toxicology / George D. Clayton, Florence E. Clayton, editors ; contributors, R.E. Allan ... [et al.].
Patty's industrial hygiene and... 1991 [GENBIB]
LC CALL NUMBER: RC967.P37 1991<SciRR> bi91-27383