

Homemade Primer Course

This document describes how to make homemade ammunition primers. Approaches to make corrosive and noncorrosive primers are covered.

W. Marshall Thompson PhD

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Warning/Disclaimer

This course discusses the creation and work with chemical compounds and mixtures that present a real risk of serious injury and/or death if mishandled. In addition, some of the chemicals discussed are toxic and present a danger to a person's health if inhaled or ingested. Primer compounds are considered to be "Primary" explosives. This designation is a result of the sensitivity of these materials to percussion, heat, and sparks (both electrical and mechanical) and their intense power during detonation. Therefore, anyone who uses this information to make primer compounds or primers does so at their own risk. The creators and instructors of this course will not be held legally liable for any accidents or injuries resulting from this information.

To avoid serious injury or death, always work with primer compounds in small quantities of less than ~2 grams (~30 grains) at a time. Always wear eye protection and work in a clutter free, well-ventilated area. It is recommended that wood, plastic, or other non-sparking tools be used to avoid accidental ignition of primer compounds and primers. Work on a non-porous surface and carefully clean up all residue and dust from the work area when finished. It is important to wash your hands thoroughly with soap and water after working with primer compounds to avoid accidental poisoning.

Is it Legal

According to current BATFE rules, making ammunition primers for your own personal use is legal (as is making your own fireworks.) Selling them or even giving them away is not legal without acquiring the appropriate Federal License(s) for manufacturing and selling explosives. Despite the absence of Federal restrictions on personal primer manufacture, there may be state regulations that affect how you store certain chemical compounds and in what quantities they may be stored. Consult competent legal advice if you are unsure of your particular situation. Be aware that making primers in your home, garage, or external workshop is likely to carry more restrictions than making them in a commercially zoned building.

So, making primers on a small scale for your own personal use is unlikely to get you into trouble. None-the-less, expect your name to appear on some government list if you purchase several of the chemicals needed to make various primer mixtures. Finally, some very useful chemicals for making primers are legally restricted by the government (e.g. Red Phosphorus) and cannot be legally purchased or possessed by individuals who do not have the appropriate licenses or work for a company that has a legitimate need for those chemicals.

How Do Primers Work

The Discovery of percussion sensitive chemicals

In the 1700's and early 1800's, a number of chemists made various compounds that were found to be sensitive to shock, heat, friction, and sparks. While many of these compounds were extremely sensitive

dangerous and unpredictable, others were more tame and although risky could be manipulated and used for various purposes such as military explosives. One such material was mercury fulminate which was easily synthesized from metallic mercury, alcohol and acid.

In general, all percussion sensitive chemicals are ignited in the same way under a sharp blow. As the material is crushed, sharp edges on some of the primer ingredients rub against one another creating friction and very localized high temperatures. When these temperatures become high enough, the reaction of the primer mixture is initiated and rapidly spreads throughout the mass generating heat, flames and incandescent particles. There is a threshold of impact energy that must be crossed to ignite a given primer mixture. This threshold energy is routinely measured by commercial primer manufacturers on every lot of primers they make to be sure they are neither too sensitive (e.g. round goes off when accidentally dropped on a hard surface) nor too insensitive to impact (e.g. misfires.)

Percussion Caps

During this same time, flintlocks were the state-of-the-art in firearms but suffered from unreliable ignition, especially in rainy or damp conditions (recall the admonition to “keep your powder dry”.) The search for a better ignition system eventually brought the shock sensitive compounds together with firearms. Percussion caps were first made and patented in the early 1800’s and were widely used until the end of the Civil War. These caps were typically composed of a copper cup partially filled with a mixture of mercury fulminate and several other chemical compounds. The caps were placed over a nipple containing a hole that led to the powder charge inside the barrel. When struck by the gun’s hammer, the primer compound exploded sending hot gases and sparks through the nipple to the powder charge causing it to ignite. This invention greatly improved the ignition reliability of muzzle loading guns.



Rimfire Metallic Cartridges

Several decades after the development of percussion caps, a self-contained metallic cartridge was designed that placed the primer compound into a deformable hollow rim. The 22 short was the first

metallic cartridge introduced in the US (1857) and continues to be commercially available to this day. Other larger caliber (up to 56 caliber) rimfire cartridges were designed and used in the Civil War and were commercially available until the early 1900's. All of these larger caliber rimfire cartridges were eventually replaced by the superior centerfire design due to the pressure limitation of the rimfire casing. The requirement to have a rim that was thin and soft enough to crush with the firing pin limited the internal pressure that these casings could safely contain without failing.



Centerfire cartridges

Shortly after the Civil War, new cartridge designs were developed to make the production of ammunition more efficient. Eventually, the current centerfire cartridge design was developed that used a separate primer located in the center of the cartridge head. A major advantage of this design was that the cartridges could be easily reloaded by replacing the fired primer with a new one, refilling the case with gunpowder, and pressing in a new bullet. Reloading tools quickly appeared allowing cowboys to reload their ammunition while sitting around the campfire in the evenings.



Mercuric primers work great but make brass brittle

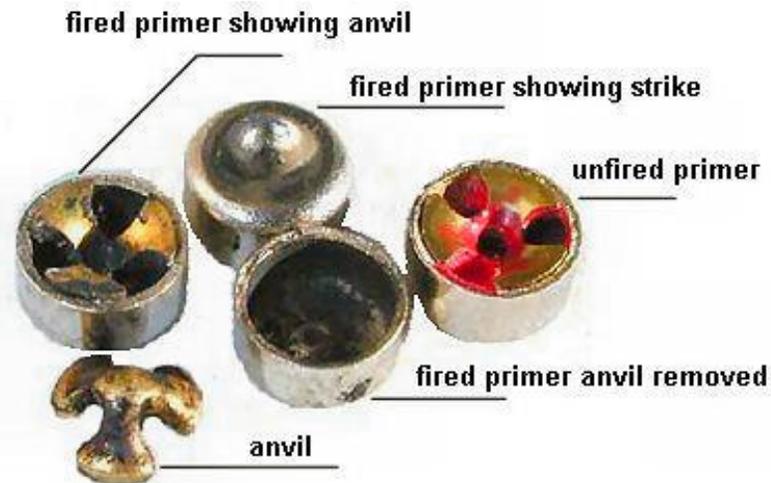
The same types of priming compounds originally used in percussion caps were still being used in the new centerfire primers. It was discovered that the cartridge brass became brittle and tended to crack when reloaded. This embrittlement was found to be caused by residues from the mercury fulminate based primers. Metallic mercury formed during the combustion of mercury fulminate selectively attacked and amalgamated the zinc in the brass alloy causing it to become brittle. Pure copper casings were briefly used to avoid this problem, however, copper was found to be too soft to hold up well to the high pressures generated during firing. Therefore, to preserve the brass for reloading a new primer compound was needed that did not use mercury fulminate. Despite the knowledge that mercury fulminate based primers ruined brass casings for reloading, non-corrosive mercuric primer formulations continued to be used in commercial ammunition until the early 1940's.

Non-Mercuric primers were developed to save brass

In the late 1800s mixtures of potassium chlorate ($KClO_3$) with various "fuels" were found to be suitable for use in primers. These mixtures were reliable and had a long storage life even under unfavorable conditions commonly encountered in military campaigns. The main negative aspect of these primers was their "corrosive" effects on steel barrels and receivers. This was especially noticed during the conversion from black powder to smokeless powder which occurred around the same time. When black powder burns it produces a large quantity of soot and other residues that coat the inside of the gun barrel. This powder residue was found to create a protective barrier to the corrosive effects of potassium chlorate primer residues. When ammunition cartridges began using smokeless powders, they burned so cleanly that no significant residues were formed inside the barrel. Therefore, the corrosive primer residues came into direct contact with the steel and rapidly caused pitting, rusting and corrosion. Since significant corrosion could occur overnight it became necessary that guns be cleaned within hours of being shot to avoid damage.

Non-Corrosive primers were developed to protect barrels

In the 1930's new non-corrosive primer formulations were developed in Europe that eliminated the requirement to clean guns quickly after shooting them. The combustion residues are non-corrosive to steel and brass. Most of these new formulations are based on lead styphnate, an explosive lead salt. More recently, some of the newer "green" primers have replaced lead styphnate with safer chemicals that do not contain toxic heavy metals. Virtually all commercially available primers today use either lead styphnate and/or lead azide as the primary explosive.



The Ideal Primer

Commercial primers are amazingly reliable devices with a failure rate of less than 1 in 3 million. It is interesting that the most important step in primer manufacture, filling the cups with primer compound, continues to be done by hand. Despite this phenomenal performance, no “ideal” primer exists today. The ideal primer should perfectly meet all of the following requirements.

Single compound

It would be great if a single pure chemical compound could be used in the primer. Unfortunately, no material has yet been found that can perform all the required functions. Therefore, all modern primer compounds continue to be composed of physical mixtures of 3 or more compounds.

Sensitive to percussion

This property is a fine line. The primer must be sensitive enough to be reliably set off by the firing pin strike, but not so sensitive to be set off by normal manufacturing and handling processes. Ever notice that accidentally dropped rounds almost never fire? This is why.

Generates hot flame/sparks

Obviously the fired primer has to generate enough energy to ignite the propellant. This is relatively easy when fast pistol powders are being ignited. Magnum pistol and most rifle powders are much slower to burn and harder to ignite. Also, some powders are susceptible to position variability when used at low fill rates unless a suitably energetic primer is used.

Insensitive to heat/humidity during storage

Ammunition is often assembled and stockpiled for years before use. The primer must not quickly degrade when the ammunition is stored in less than ideal conditions. Commercial primers are calculated to last at least 150 years when stored under normal temperature/humidity conditions. I am personally aware of ammunition made in the 1870s that has been shot in 2014 without any problems (i.e. no

misfires or squibs.) Today's primer compounds are even more stable to storage than the typical mercury fulminate based primers made in the 1870s. The main exception for primer stability are some of the new "green" primers. Some of these are known to have problems with a short storage life.

Safe to manufacture/handle

In this case, safe is only a relative term as any primer formulation that is sensitive enough to use in ammunition will inherently be risky to make and handle. It is hard to appreciate the tremendous amount of energy released by the tiny amounts of primer compound used in an ammunition primer. A teaspoon of primer compound is easily enough material to cause serious injuries, damage or a fatality should it unexpectedly explode. Commercial primer manufacturers know that even with the best possible precautions and safety procedures, an accident will occasionally occur during primer production. These companies manage this risk by using small batch sizes of primer compound (they typically work with 1-5 lb batches) working in reinforced blast proof buildings and only allowing a few employees to work in the building at a time. Despite these precautions fatalities still happen but are thankfully rare. Primers can tolerate a surprising amount of abuse when slowly deformed (i.e. staying below the threshold energy for ignition.) However, an accidental stray spark of static electricity could easily cause an entire batch of primer compound or prepared primers to go off with disastrous results. There is a good reason why special HazMat fees are charged to ship primers. In summary, no compound that is shock sensitive enough to be successfully used in primers will be totally free of explosion risks during its manufacture or handling.

Non-toxic

Because of the use of lead styphnate and other heavy metal salts, modern commercial primers create various hazardous residues during combustion. This is normally not a problem when good ventilation is present and exposure is infrequent. However, workers at indoor shooting ranges can sometimes be exposed to enough lead in the air to cause health problems. This was the main reason for the creation of "green" (i.e. no heavy metals) primers. Interestingly, the non-mercuric but corrosive primer compounds used in the late 1800s are much safer for your health since no heavy metal salts were used.

Basic Types of Primers

The primer compound is a mixture of materials performing one or more of the following functions: 1) initiator, 2) oxidizer, 3) fuel, 4) sensitizer, 5) frictionator, and 6) binders. There are 4 general classes of primer compounds, each with their own advantages and disadvantages.

Mercuric/Corrosive

This class represents the original compounds developed for percussion caps. These primers have a good balance of energy and sensitivity and are simple to make. The combustion residues are corrosive and require prompt cleaning of the gun after using it with these primers. As noted before, the use of mercury fulminate made brass cases brittle so they could not be safely reloaded.

Mercuric/Non-Corrosive

Once the corrosive nature of the older mercury fulminate primer compounds was recognized, other formulations were developed that while still using mercury fulminate, were no longer corrosive. These primer compounds still ruined the brass cases for reloading, but they no longer corroded steel barrels. Primers using this type of compound continued to be available until the start of WW2.

Non-Mercuric/Corrosive

In the late 1800s, the US military decided they wanted to reload their fired casings to save money on ammunition. A new primer compound that was non-mercuric was developed that did not harm the brass, but was also found to be corrosive. These primer formulations are mostly based on potassium chlorate mixtures. It was not until the early 1920s that the corrosive residue attacking the steel was identified as potassium chloride. The damage to the gun barrel can be easily prevented by washing out the corrosive salts using hot water. This cleaning procedure was routinely used by all soldiers until about 1950 when all military ammunition was converted to non-corrosive primers.

Non-Mercuric/Non-Corrosive

All modern commercial primers are of this class. Most of these primers are based on lead styphnate, although some use lead azide. Except for the new “green” primers, all of these primer mixtures generate toxic heavy metal salts during combustion.

Reliable Homemade Primers

Of all the techniques and methods available to make homemade primers, only three are considered feasible for the average non-chemistry trained reloader. Regrettably, all of these methods produce primers of the non-mercuric/corrosive type and require the tried and true hot water cleanup procedures to avoid damaging your barrel.

Preparation of primer cups

It is entirely possible to make your own primer cups from sheet brass if you are a machinist or are able to have the special dies custom fabricated. The needed technical drawing for making these dies can be found in the “Making Ammunition” reference book noted in the appendix.

It is more convenient to reuse previously fired primers (you have been saving them, right?). However, they must be properly cleaned and prepared for reuse. The steps below show my technique for preparing the primers.

1. Fill a rock tumbler drum about 1/3 full of used primers. Fill with water to about 2/3 full and add a squirt of dish detergent. Seal up the drum and tumble for about 30-60 minutes. Pour off the dirty water, rinse the primers and repeat the cleaning operation 2 more times. This will remove virtually all of the toxic lead salts from the primers and make them clean and shiny.

2. Pour out the clean damp primers onto paper towels, spread them out into a single layer and allow them to drain and dry overnight.
3. Next remove the anvils from the primers by holding the primer with a pair of needle nose pliers and using a sharp pointed awl or similar tool get under a leg of the anvil and pop it out. With a little practice, you can do this quickly and easily without losing the tiny anvils. Remove any paper residue (i.e. the foil) you may find that sometimes remains in the primer cup. Discard any primers that are excessively distorted or flattened. It has been my experience that large rifle primers can rarely be reused due to excessive flattening.
4. Using an appropriate sized flat punch or flattened nail, set the primer on an anvil or other smooth metal block and punch out the firing pin dimple. It is rare for the firing pin dimple to be completely removed during this operation since the metal can flow under the firing pin and be slightly thinner than the surrounding areas. Discard any primers that have an especially heavy primer strike or are pierced.
5. Store the prepared primer cups until ready for reloading.

I recommend keeping SR and LR primers separate from SP and LP primers. This will avoid problems with misfires in pistol cartridges due to the thicker primer cups used in rifle primers. Sometimes they work and sometimes they don't or require multiple strikes to get them to fire. The same issue would exist if you were to use new rifle primers in pistol cartridges. The firing pins in pistols are not able to strike the primers as hard as a rifle does.

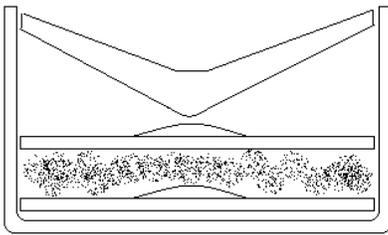
Primers made from toy caps

This method is the easiest, safest and least likely to get you on a federal watch list. On the other hand, the resulting primers are not very energetic and may fail to reliably ignite some powders. The best toy caps to use are made in Germany and can be found under various brand names at Walmart or at Dollar General. The caps made in China are inferior for use in cap primers. Don't waste your money buying them. Here are the steps for making cap primers:

Materials needed: a) leather punch or handheld 1/8" paper hole punch, b) rolls of good quality caps, c) bamboo skewer, d) fast pistol powder

1. Using a leather punch, cut out a number of cap blisters from the roll of caps to the appropriate size to fit inside of the primer cups you are reloading. For SP primers, I have found that hand held paper hole punches that make 1/8" holes will work well. As much as possible, try to center the cap blister in the punched out circle. Expect to accidentally set off a few caps while doing this operation. If you do pop off a cap or two, carefully wash the punch when you have finished with hot water or the punch will quickly start to rust from the corrosive cap residue (i.e. just like your gun barrel.)

2. Place one cap circle inside of a prepared primer cup with the blister facing up and carefully pack it down with the end of a bamboo skewer.
3. To give the primer a little more energy, sprinkle a thin single layer of fine gunpowder over the cap. Bullseye is an excellent choice, but any fine grained pistol powder will work. I have a cup of scrap gunpowder I use for this purpose that was recovered from live rounds I occasionally find in the brass box at the range.
4. Place the second cap circle, blister side up, over the gunpowder and carefully pack it down with the bamboo skewer.
5. Finally, place a saved anvil over the cup pointy end down and carefully/slowly push it into place using the side of your needle nose pliers. Even being very careful, I typically pop off about 1 out of 20 primers during this operation. If that happens, disassemble the primer, clean the cup and reload with new caps and gunpowder. Once assembled, the primer is ready for immediate use. To avoid accidentally popping the caps, it is possible to desensitize them by lightly moistening them with 90% isopropyl alcohol before pressing in the anvil. After the alcohol and water evaporates (at least several hours or leave overnight to be sure they are dry) the caps become sensitive again and will work like normal.

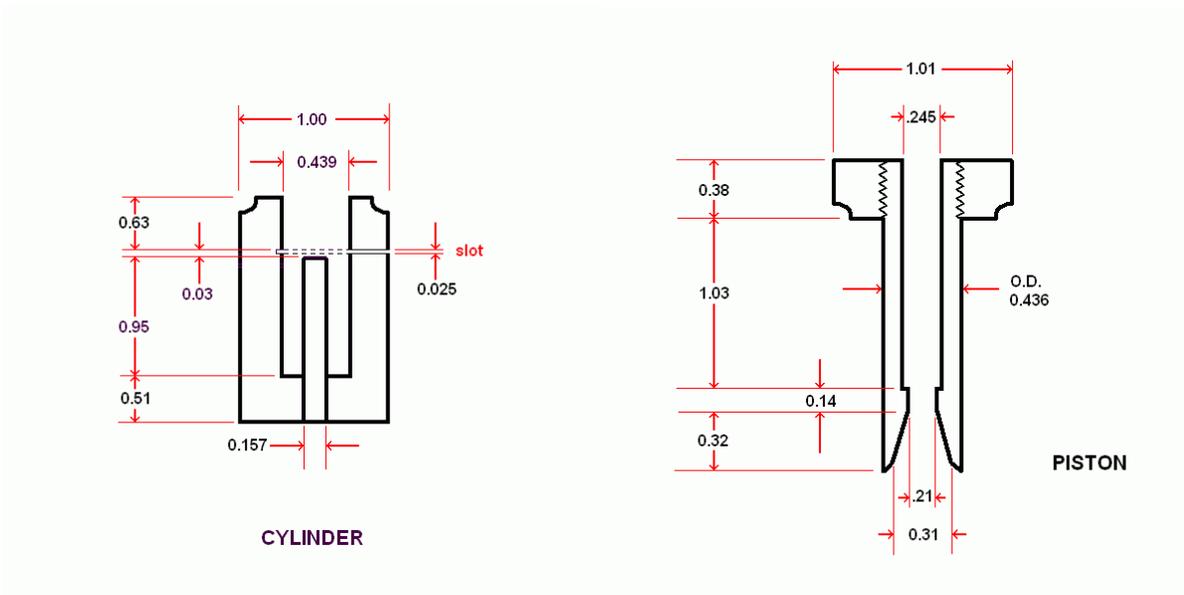


6. Save your completed primers in an empty primer box, or use them as normal in making ammunition. Any difficulties in getting the primers to seat properly can usually be traced to a distorted primer cup. The more discriminating you are when sorting out questionable primer cups, the less likely you are to have any problems seating the reloaded primers. It is rare to have a cap primer pop during normal seating in a casing but it does occasionally happen. When made correctly these primers have excellent reliability. With good consistent assembly techniques, less than 1 out of 1000 cap primers will typically be expected fail. In most cases I have analyzed, the cap primer was found to have fired, but was not energetic enough to set off the gunpowder. These primers have successfully set off powders as slow as IMR 4895 used in 223 Remington cartridges.
7. The cost of making cap primers is quite low (\$0.003/primer) compared to commercial primers (\$0.04/primer), or about a 10:1 cost advantage.

It is possible to make percussion caps using toy caps. A tool called a tap-o-cap was marketed by Forster several years ago that can stamp out and make #11 percussion caps from aluminum drink cans. Although this tool is out of production, it can occasionally be found for sale on eBay.



If you are handy in the machine shop, you can make a similar tool using these mechanical drawings:





Primers made from strike-anywhere matches

This method is easy, relatively safe and unlikely to get you on a federal watch list. In fact, this is the method that the military teaches its troops for making improvised ammunition (see TM 31-210, *Improvised Munitions Handbook*.) The resulting primers are more energetic than cap primers, but still significantly less than commercial primers. The main problem with this method is finding good strike anywhere matches. The only part of the match that is used to make the primer is the white tip which seems to have shrunk in recent years. The only ones readily available are from Diamond which are green with a small white tip. It takes 3-4 matches to make a single SP primer. Here are the steps for making cap primers:

Materials needed: a) Strike anywhere matches, b) razor blade or sharp knife, c) hammer (optional), d) bamboo skewer (optional),

1. Working on a non-porous surface, carefully cut off the white tips of 3-4 matches using a razor blade or sharp knife. For safety and because it is so easy to set this compound off, only process enough matches at a time to make one primer. Only the white part is wanted, so be careful to only remove this part of the match.
2. Using the flat face of a hammer and a rolling motion, carefully crush the white compound into a fine powder. Alternatively, use the razor blade to chop the white tips into a powder.
3. Fill a primer cup with the loose white powder and pack the powder tightly using the end of one of the match sticks or a bamboo skewer. Add more powder and repack until the cup is 1/2 to 5/8 full of packed powder.
4. Finally, place a saved anvil over the cup pointy end down and carefully/slowly push it into place using the side of your needle nose pliers. As with the cap primers, lightly moistening the match powder with 90% isopropyl alcohol will help avoid accidental ignition while pressing in the anvil. After the alcohol and water evaporates (at least several hours or leave overnight to be sure they are dry) the match primers become sensitive again and will work like normal.
5. Save your completed primers in an empty primer box, or use them as normal in making ammunition. When made correctly these primers have excellent reliability. The main disadvantage is the slow preparation technique. It can easily take 5-10 minutes to prepare a single primer.

6. The cost of making match primers is low (\$0.015/primer) compared to commercial primers (\$0.04/primer), or about a 2:1 cost advantage.

As with toy caps, it is possible to use this method to make/reload percussion caps.

Primers made with H-48 compound

This method uses a real primer compound and carries some safety risks. It is also likely to get you on a federal watch list since several chemicals common to the fireworks industry must be purchased. The resulting primers are as energetic as commercial primers and should reliably ignite all powders. A few modifications to the formulation can further improve the stability and reliability of the primer. Here are the steps for making H-48 primers:

Materials needed: a) Potassium Chlorate powder, b) Antimony Sulfide powder, c) Sulfur powder, d) finely ground glass preferably pyrex (consistency of flour) or grit, e) Sodium Bicarbonate powder (i.e. baking soda), f) Scale that weighs in grains, g) plastic weighing boats, h) SS or plastic spatula for transferring chemicals, i) plastic spoon, j) bamboo skewer with a flat end and a powder scoop carved on the other end, k) paper disks punched out of ordinary copy paper that will fit inside the primer cup, l) dilute shellac solution in denatured ethyl alcohol (~1 part shellac in 10 parts of alcohol but the exact concentration is not critical), m) Aluminum powder (60-100 mesh) optional, n) needle nose pliers, and o) small rod or tiny screwdriver (diameter of shaft ~1/16" or smaller)

1. Using 4 plastic weigh boats and a suitable scale, weight out the following materials:
 - a. Boat 1, 17.0 grains of potassium chlorate,
 - b. Boat 2, 9.0 grains of antimony sulfide,
 - c. Boat 3, 4.0 grains of ground glass, and
 - d. Boat 4, 3.0 grains of sulfur, 0.2 grains of sodium bicarbonate (helps stabilize the mixture on extended storage) and 0.2 grains of aluminum powder

The aluminum powder is optional, but provides extra incandescent particles to help ignite slower gunpowders. Aluminum powder is commonly used in commercial Magnum primers for this same purpose.

2. Put ingredients "b", "c", and "d" on a plain 8 1/2 x 11 sheet of paper and mix thoroughly using the back side of a plastic spoon. The pile of powder may also be rolled back and forth on the paper to aid in blending the ingredients. These ingredients (and only these ingredients) are safe to mix together without special precautions. *****IMPORTANT: DO NOT ADD ingredient "a" until instructed below*****
3. Collect the thoroughly mixed powder from above into a single pile by lifting up the edges of the sheet. Now pour ingredient "a" into a separate pile on a clean area of the sheet that is beside

but not contacting the previous pile. Using the backside of the plastic spoon, crush any lumps in ingredient "a" and make a smooth free flowing powder. **DO NOT MIX ingredient "a" with the other ingredients until this crushing step is completed.**

4. Now, lift up the edges of the paper sheet and roll the two piles of powder into one another. Once these powders are combined, the mixture becomes explosive so be very careful to avoid sparks or any rapid crushing action. Using only this rolling action on the paper sheet, continue to mix the powders until a homogeneous mixture is formed. The backside of the plastic spoon can be used to gently breakup any agglomerated lumps of powder that are found during this blending step. The final result is ~33 grains of light gray powder that is H-48 primer compound. It may be stored in a small plastic condiment cup with a snap on cap until ready for use. This amount of primer compound is sufficient to make ~100 SP primers or ~60 LP primers. The H-48 primer compound can be tested (preferably outside) by placing a small amount (about what fits in a SP cup) on a smooth metal surface and striking it with a hammer. Properly made H-48 compound will explode with a report about like a large firecracker and can make your ears ring for several minutes. With that in mind, consider the potential power of a full 33 grain batch going off (~100 times what you just set off!) Respect the primer material and work safely to prevent accidents. *****WARNING! DO NOT MAKE OR STORE LARGER AMOUNTS OF H-48 PRIMER COMPOUND*****
5. Position 10-25 prepared primer cups onto the edge of a 6" x 6" sheet of waxed paper. In the middle of the sheet, pour out about 1/4 of the batch of primer compound made previously and recap the container. Using the carved bamboo scoop, position an empty primer cup next to the pile and add H-48 primer compound until the cup overflows. Using the side of the scoop, remove the excess powder so that the powder is level with the top of the cup. Move this filled cup to the edge of the wax paper sheet and repeat the operation until all of the cups are filled.
6. Using the bamboo skewer with a flattened end, position a filled cup close to the edge of the wax paper sheet and carefully pack the powder tightly. The cup will be ~1/2 full of packed powder when this step is completed. This is exactly the correct amount of powder that needs to be used in the primer and is why I prefer the dry packing method. It is ~21 mg or ~0.3 grains of primer compound in a SP primer. LP primers will contain ~35 mg or ~0.5 grains of H-48 compound. It is possible to refill the 1/2 full cups with H-48 powder and repack to make them 3/4 full. While this will make a more energetic primer, it is very difficult to install the anvil when the cup is this full. Repeat this operation until all of the cups are packed.
7. Place a paper disk over the packed H-48 compound in each cup and pack the powder one more time. Moisten the primer pellet with dilute shellac in ethyl alcohol solution using a small pointed rod or tiny screwdriver to transfer small drops of solution to the cup until the paper disk just stays moist (don't overdo it.) This step desensitizes the primer compound so that the anvil can be safely installed and binds the powder into a solid pellet once the alcohol dries. This moistening step is critical in making reliable H-48 primers. Place a saved anvil over the cup pointy end down and carefully push it into place using the side of your needle nose pliers.

Finally, move the completed primers to a well-ventilated area so that the alcohol can completely evaporate (overnight works well).

8. Save your completed primers in an empty primer box, or use them as normal in making ammunition. When made correctly these primers have excellent reliability and energy (very close to commercial primers.) This same technique can be used to reload berdan primers, minus the anvil step. It takes about 30 minutes to process 25 primers from start to finish. Completed H-48 primers have about the same stability/sensitivity as standard commercial primers.
9. The cost of making H-48 primers is very low (\$0.0003/primer) compared to commercial primers (\$0.04/primer), or about a 100:1 cost advantage.

With slight modifications, this method is commonly used to make/reload percussion caps. In many cases, the primer mixture is wet loaded into the cups. The alcohol/shellac binding solution is used to moisten the H-48 compound until it is the consistency of toothpaste. The percussion cups are filled ~1/2 way with this mixture and a paper disk installed. Allow the alcohol to dry and the percussion caps are ready for use.

Making Non-Mercuric/Non-Corrosive Primers

Based on recent work, methods for making several safe and reliable non-mercuric/non-corrosive primer mixtures have been developed. Be aware that this is an advanced topic in which a good working knowledge of chemistry is useful although it is not absolutely required. Every non-corrosive formulation presented requires at least one raw material that cannot be purchased and must be synthesized by you. This is not just a burden for the individual primer maker since commercial primer manufacturers must also synthesize certain materials on site as they are not stable enough to safely transport by commercial carriers. Synthesis methods are included in the discussions, but it is recommended that more thorough research be conducted to learn more about these compounds and to look at alternative synthesis methods that may work better for your particular situation (i.e. available raw materials.) Depending on what raw materials you can obtain, it may be necessary to go back several steps in a synthesis chain in order to obtain a certain final product (e.g. urea -> guanidine -> guanidine nitrate -> nitroguanidine -> aminoguanidine bicarbonate -> tetrazene.) Therefore, in some cases distant precursor chemicals must be purchased and a fair amount of wet chemistry is required. It helps if you have laboratory glassware for these reactions, however, it is perfectly possible to use readily available home glassware (i.e. a mason jar) to do this work. If you are willing to do a little home chemistry, this option is available to you.

Primers made with Lead Nitratohypophosphite.

Information available in US patent 4432819 describes a rimfire primer formulation that consists of: a) Lead nitrate, b) Lead hypophosphite, and c) Glass powder. These two lead salts react with each other in aqueous solution to produce a well known explosive double salt called lead nitratohypophosphite. This double salt has been used in various primer formulations since the early 1900's. The innovative part of this patent is that the 3 dry ingredients can be safely mixed, stored and used to charge rimfire cases with no danger of explosion since none of these individual ingredients are explosive or sensitive to

percussion. Once the mixture is moistened with water, the reaction to form lead nitratohypophosphite proceeds quickly (~1-2 minutes). While still moist, the mixture continues to be safe to handle. However, once it dries, the primer compound becomes sensitive to percussion. Testing in rimfire and centerfire rounds shows that these formulas give excellent performance although they are slightly less powerful than standard commercial primers. Typical formulations that work very well are:

EPH 0 (rimfire formula)

	%	grains
Pb(H ₂ PO ₂) ₂	40.0	13.2
Pb(NO ₃) ₂	40.0	13.2
Glass	20.0	6.6

EPH 10 (centerfire formula)

	%	grains
Pb(H ₂ PO ₂) ₂	20.0	6.6
Pb(NO ₃) ₂	20.0	6.6
Ba(NO ₃) ₂	39.0	12.9
CaSi ₂	11.0	3.6
PbO ₂	5.0	1.7
Sb ₂ S ₃	5.0	1.7

The main downside of this approach is that there are no commercial sources of lead hypophosphite, so you must synthesize this chemical yourself. Fortunately, the synthesis is trivial and can be easily done at home using normally available glass containers. Another downside is that lead nitrate is a poison and must be handled carefully to prevent inhalation of any dust or ingestion. Wash thoroughly every time after making or using this primer mixture.

Materials needed to make Lead Hypophosphite: a) Calcium Hypophosphite or Sodium Hypophosphite (these chemicals can be purchased on eBay for between \$25-40/lb.) The sodium salt tends to be cheaper and the end result is the same, b) Lead Nitrate (this can be purchased from Elemental Scientific for ~\$20/lb + a \$25 hazmat fee), c) Scale that weighs in grams, d) plastic weighing boats, e) SS or plastic spatula for transferring chemicals, f) Gravity or vacuum filtration setup.

Using 2 plastic weigh boats and a suitable scale, weight out the following materials:

- a. Boat 1, 17.0 grams of Calcium Hypophosphite or 21.5 grams of Sodium Hypophosphite,
- b. Boat 2, 33.1 grams of Lead Nitrate,

In 2 separate suitable glass containers, dissolve the Lead Nitrate into ~50 ml of very hot distilled water, and the Calcium/Sodium Hypophosphite salt into ~150 ml of very hot distilled water. While keeping both solutions hot (almost boiling) slowly add the Lead Nitrate solution in small portions to the Hypophosphite solution with good stirring. Adding dropwise with a medicine dropper works well.

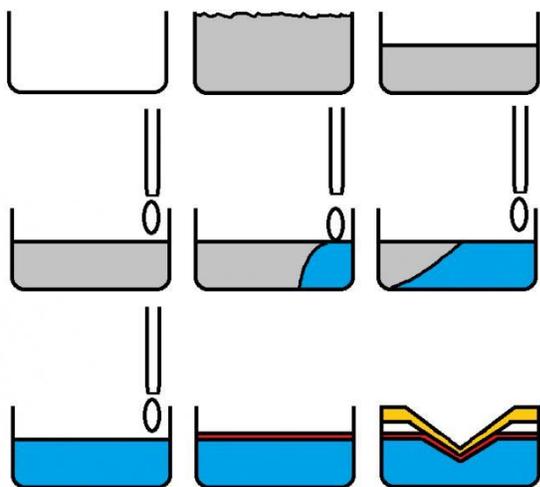
****WARNING** This order of addition is absolutely critical!!!** If the order of addition is reversed, dangerously explosive Lead Nitratohypophosphite is formed instead of the desired Lead Hypophosphite. **Do not make this extremely dangerous mistake!!!**

As the Lead Nitrate solution is added, Lead Hypophosphite is formed and precipitates as a fine white powder which stays suspended in the swirling solution. Once all of the Lead Nitrate has been added continue to stir for several minutes and then cool the container and solution in an ice water bath until its temperature falls to or below 5°C. This will cause the maximum amount of Lead Hypophosphite to precipitate for recovery. Filter the cold solution to collect the solid. The filtrate may be washed with a minimum amount of ice cold distilled water to remove any residual Calcium/Sodium Nitrate by-product that may be trapped in the precipitant.

Caution: Lead Hypophosphite is slightly soluble in water so over washing will result in a loss of material.

Completely dry the white Lead Hypophosphite powder in the open air or at a maximum temperature of 40°C. Store in a clean air tight plastic container. If desired, the waste filtrate solution collected earlier can be evaporated to recover the calcium/sodium nitrate by-product which can be useful for other purposes (e.g. making black powder).

To make primers, combine the dry powders at the specified percentages given in the EPH 0 and EPH 10 formulas and blend/mix them well in a non-porous mortar and pestle. It is safe to handle this dry mixture without fear of an explosion. However, you should carefully avoid contamination of working surfaces/containers/hands due to the poisonous nature of the lead salts. Always wash your hands after using these mixtures to avoid accidental ingestion and lead poisoning. Next dry pack primer cups as normal and compress the powder into a pellet. Next, completely moisten the pellet with a 50/50 blend of water/alcohol solution. The alcohol is added to the water to break down the surface tension which allows the water to wet the powder more easily. After much trial and error, the best technique for doing this is shown in the picture below:



The trick is to allow the water/alcohol solution to flow across the pellet using capillary action until a wet sheen appears on the surface. No additional water is needed after that point. A paper foil is added and pressed into place, and then the anvil is mounted pointy end down. If done quickly (i.e. within 1 minute after wetting) the mixture is still plastic and will easily flow around the anvil. If you delay too long, the pellet hardens due to the formation of interlocking Lead Nitratohypophosphite crystals and it will be much more difficult to press the anvil into place. This behavior is actually a great advantage since the mixture is self binding and provides a solid pellet that crushes well and delivers very reliable ignition. The completed primers are then allowed to dry; either 2-3 days at room temperature, or for 1-2 hours at 45-50°C (113-122°F). A thermostatically controlled block heater, commonly used to incubate test tube cultures works very well for this purpose.



This particular unit was picked up on eBay for \$19.99 + shipping. The test tube holder block is flipped upside down so that the flat bottom can be used to set the primers on for drying. The 2 cases on the block are berdan primed cases that are drying after pressing in moist berdan primers. It also works great to dry reprimed rimfire cases.

Once dry the primers are active and can be used as normal in reloading ammunition. Reliability of primers has been essentially 100%.

Primers made with Tetrazene.

Tetrazene is a well known primary explosive that has been used in primer formulations since the earliest days of non-corrosive primers. However, until recently, its normal use has been as a sensitizer with a loading of only 2-5%. Information available in US patent 8052813 by Cheddite describes a shotgun primer formulation that consists of: a) 15-25% Tetrazene, b) 40-60% Barium Nitrate, c) 18-30% Antimony Sulfide, and d) 5-12% Aluminum powder. Testing of the following formulation based on the patent disclosures gave interesting results.

EPT 0 (centerfire formula)

	%
Tetrazene	20.0
Ba(NO ₃) ₂	48.0
Sb ₂ S ₃	24.0
Al	8.0

While this formula would work in shotgun (~65 mg of primer mixture) and large pistol primers (~40 mg of primer mixture), it failed in small pistol primers (~20 mg of primer mixture). It seems that there is a required threshold amount of primer mixture in the cup before these primers function properly.

Further testing on modified versions of the tetrazene formulation identified EPT 3 as a formulation that works well in all primer types (i.e. SP, LP, SR, LR, Shotgun, and 5mm berdan).

EPT 3 (centerfire formula)

	%	gr
Tetrazene	40.0	13.2
Ba(NO ₃) ₂	32.0	10.6
Sb ₂ S ₃	20.0	6.6
CaSi ₂	8.0	2.6

You will have to synthesize Tetrazene in order to make these primers. While the synthesis of tetrazene is relatively easy, getting the needed raw materials is not. The Aminoguanidine bicarbonate used in this synthesis was obtained from Santa Cruz Biotech and cost ~\$100/lb with added hazmat fees and special hazmat packaging. If you have access to a wet laboratory, it is not too difficult to make this raw material starting with guanidine nitrate which can be obtained from Pyro Chem Source for \$8/lb. If you are interested, see US patent 1990511 for information on this synthesis. Here is a method of making tetrazene from aminoguanidine bicarbonate.

9.5 g of NaNO₂ (sodium "nitrite") is added to a solution of 13.6 g aminoguanidine bicarbonate in 125 ml water and 50 ml of white vinegar (5% acetic acid). The precipitation of tetrazene starts after a couple of hours of standing and is finished after ~24 hours. Yield is ~9.5 g which is about 50% of theoretical. The light yellow precipitant is collected by filtration and washed with several small portions of distilled water. The tetrazene filter cake is completely dried at room temperature for several days and then stored in a clean air tight plastic container.

To make primers, combine the dry powders at the specified percentages given in the EPT 3 formula and then gently "wet mix" them well in a non-porous mortar and pestle using a minimum amount of 90% isopropyl alcohol as the wetting agent. After mixing, spread the resulting paste on a non-porous surface (e.g. a glass plate) to dry. Once dry, gently crush the material back into a powder and store in an air tight plastic container. This primer mixture is complete and active after mixing and should be handled with care to avoid accidental detonation. Personal experience has shown that it is less sensitive to handling and percussion than H-48 primer mixture but it still must be respected. The EPT 3 powder is dry packed

into primer cups, a paper foil added and an anvil pressed into place pointy end down. Optionally, you can moisten the primer pellet with dilute shellac in ethyl alcohol solution to bind the pellet. However, while this step “may” increase the reliability of the finished primers, those made without binder solution seem to work just as well and do not require a time consuming drying step.

If the primers are made without adding the binder solution they are ready for use immediately after seating the anvil. Tetrazene based primers have several advantages over other formulations: 1) in addition to being non-corrosive, they are also non-toxic since no lead salts are used, and 2) they burn exceptionally cleanly. Typically, the only residue left in the cup after firing are small scraps of paper from the paper foil. On-the-other-hand, although they reliably set off all pistol rounds tested so far, they are not as powerful as commercial primers and have little observable flash. Attempts to improve the firing temperature and flash of this type of formulation by adding aluminum powder were not successful.

Primers made with Styphnic Acid.

This method makes primers that are essentially identical to commercial primers using the patented (now expired) Eley prime technique. Normally, styphnic acid (aka trinitroresorcinol or TNR) is reacted with various lead salts to make treacherously sensitive lead styphnate which is then mixed with other primer ingredients to make a wet paste. This paste is wet loaded into primer cups which after assembly and drying become the ubiquitous primers we buy. Despite having some of the best safety equipment and methods available, commercial primer manufacturers have occasional accidents while making and using lead styphnate. It is not a matter of if an accident will happen, but when. The Eley Prime technique greatly improves the safety of making these primer mixtures by forming the lead styphnate *in-situ* after the primer cup has been filled with an inert mixture of dry powders. An Eley Prime type formulation that gives excellent performance is EPS 5 which is shown below.

EPS 5 (centerfire formula)

	%	gr
Styphnic Acid	20.0	6.6
PbO	18.0	5.9
Ba(NO ₃) ₂	39.0	12.9
CaSi ₂	11.0	3.6
PbO ₂	5.0	1.7
Sb ₂ S ₃	5.0	1.7
Tetrazene	2.0	0.7

This dry mixture is completely safe to make and handle. When water is added, the styphnic acid and lead oxide react to form lead styphnate which becomes sensitive to percussion after drying. It should be noted that tetrazene is also used but in its normal role as a sensitizer.

Here is a method for making styphnic acid from resorcinol (available from Elemental Scientific for ~\$60/lb), sulfuric acid and ammonium nitrate. ****WARNING** This reaction must be done in a fume hood, or outside in a well ventilated area.**

Put 50 ml of concentrated H₂SO₄ into a 500 ml Erlenmeyer flask, add 11.0 gram powdered resorcinol and stir until dissolved. Heat mixture to 100°C for 30 minutes during which time it becomes a pink cream. Cool to -5°C and add 25 gram NH₄NO₃ in small portions over a period of 5-10 minutes. Large quantities of toxic red NO₂ are generated as nitric acid is generated *in-situ* and reacts with the sulfonated resorcinol intermediate. After the initial reaction has subsided, heat the mixture to 100°C for 1 1/2 hours to complete the reaction. Allow the mixture to cool and then add ~100 ml of ice cold water. The styphnic acid will precipitate as a fine powder. Cool the mixture to 5°C and then quickly vacuum filter the solution. Rinse the crystals with ~450 ml of ice cold water to remove residual acids and any (NH₄)₂SO₄ by-product that might be present. While the resulting styphnic acid is quite pure enough for use in primers, if a purer product is desired the crude styphnic acid can be recrystallized from 2:1 water/ethanol solution. Use 8 ml/gram of styphnic acid. After completely drying the styphnic acid at room temperature store it in a clean air tight plastic container. Be warned that styphnic acid is powerfully staining intense yellow material which will stain almost anything it contacts including your skin. Fortunately, it dissolves readily in a solution of sodium bicarbonate which makes cleanup much easier.

To make primers, combine the dry powders at the specified percentages given in the EPS 5 formula and blend/mix them well in a non-porous mortar and pestle. It is safe to handle this dry mixture without fear of an explosion. Dry pack primer cups as normal and lightly compress the powder into a pellet. Next, completely moisten the pellet with a 50/50 blend of water/alcohol solution to initiate the lead styphnate reaction. Complete the buildup of the primers with the addition of a paper foil and anvil. The completed primers are then allowed to dry; either 2-3 days at room temperature, or for 1-2 hours at 45-50°C (113-122°F). The dried primers have exactly the same power and flash as commercial primers.

For rimfire cases the following formulas have been made:

Rimfire Formulation EPS 0

	%	gr
Styphnic Acid	21.6	7.1
PbO	19.9	6.6
Ba(NO ₃) ₂	20.0	6.6
Tetrazene	3.5	1.2
Glass	35.0	11.6

Rimfire Formulation EPS 2

	%	gr
Styphnic Acid	24.9	8.2
PbO	23.0	7.6
Ba(NO ₃) ₂	22.5	7.4
Tetrazene	4.6	1.5
Glass	25.0	8.3

50%EPHO/50%EPSO

Rimfire Formulation EPM 4

	%	gr
Styphnic Acid	10.8	3.6
PbO	10.0	3.3
Ba(NO ₃) ₂	10.0	3.3
Pb(H ₂ PO ₂) ₂	20.0	6.6
Pb(NO ₃) ₂	20.0	6.6
Tetracene	1.8	0.6
Glass	27.5	9.1

Rimfire Formulation EPM 11

	%	gr
Styphnic Acid	10.8	3.6
PbO	10.0	3.3
Ba(NO ₃) ₂	10.7	3.5
Pb(H ₂ PO ₂) ₂	20.0	6.6
Pb(NO ₃) ₂	20.0	6.6
Tetracene	3.5	1.2
Glass	25.0	8.3

Primers made with Picric Acid.

References to primer mixtures made using lead picrate as the primary explosive can be found in patents and a few other documents from the 1930's. That primers made with this compound were not pursued commercially can be explained by the superiority of primers based on lead styphnate. However, that does not negate the fact that perfectly acceptable primers can be made with lead picrate. Picric acid is chemically similar to styphnic acid and forms percussion sensitive lead salts. Also like styphnic acid, the lead salts of picric acid can be made in 2 chemically distinct forms: 1) "normal" lead picrate and 2) "basic" lead picrate. However, while both the normal and basic forms of lead styphnate are useful in primers, only the basic form of lead picrate is sensitive and energetic enough to be used in primers. Tests attempting to make viable primers from Normal lead picrate (i.e. picric acid + lead oxide) using the Eley Prime method were unsuccessful, with primers giving only a weak fizzle.

Basic lead picrate is typically synthesized from an alkali metal picrate salt and lead nitrate. While lead picrate is less sensitive to shock and ESD than lead styphnate a significant risk remains of accidental ignition. From my research, an Eley Prime version of a lead picrate primer has never been attempted before. None-the-less, there is no reason to think that it would not be successful.

One significant advantage of picric acid based primers is that picric acid can be readily synthesized in high yield from common over the counter materials that will not draw undue attention. Picric acid can be made from:

1. Aspirin (either purchased pure as veterinarian aspirin or ground up tablets that have been purified by recrystallization to remove any binders),
2. Stump Remover (i.e. potassium nitrate), and
3. Rooto drain cleaner (i.e. conc H₂SO₄)

There are plenty of methods that can be found on the internet for doing this synthesis. Here is one that I have personally used:

Picric Acid Synthesis

Procedure:

1. Weigh out 36 gm of aspirin powder (veterinarian grade powder without binder).
2. Add the aspirin to a 500ml flask filled with 175ml conc sulfuric acid. Heat the beaker gently and stir with a magnetic stirrer to dissolve the aspirin. Remember to do this outside or in a well ventilated area.
3. When all the crystals have dissolved, heat the solution to 75-95°C and add 83g of potassium nitrate. Do this very slowly, a few grams at a time. Each time you add some, it will bubble and heat up. Wait until this reaction subsides before adding more. During the addition of the last 1/3 of the potassium nitrate, significant foaming will occur as the final nitro group is added to the aromatic ring while displacing the carbonyl group as CO₂ gas. The reaction needs to be run at an elevated temperature to avoid an induction period and assure a smooth nitration.

NOTE: This reaction produces small amounts of the fatally toxic gas, nitrogen dioxide. It MUST be run in a fume hood or outside to avoid breathing these dangerous fumes.

4. Once all the potassium nitrate has been added, heat the mixture to 120°C and keep it there for 5 minutes to complete the nitration. Then slowly let the acid solution cool to room temperature, while stirring it gently. When it has cooled, carefully pour it into a bucket of ice water (caution: conc H₂SO₄ can spatter on contact with water), to precipitate the picric acid.
5. Filter this carefully to collect the crude picric acid crystals. Be careful handling the solution or collected crystals as picric acid is highly staining.
6. Recrystallize the crude picric acid from hot water to obtain pure picric acid as pale yellow crystals. The water solution can be concentrated to obtain a second crop of pure material.

Potassium Picrate Synthesis

Procedure:

1. Dissolve a few grams of picric acid in a minimum amount of hot water.
2. To this solution, slowly add potassium carbonate (or potassium bicarbonate) to the solution until the evolution of CO₂ ceases.
3. Allow the mixture to slowly cool to precipitate potassium picrate as a fine powder.
4. Collect the potassium picrate by filtration rinsing the material with ice cold water. The filtrate can be concentrated to obtain another crop of crystals. As with picric acid, potassium picrate and its solutions are very staining.

After synthesizing the potassium picrate, it was used to make the following primer compounds. For centerfire, use EPP9 which is based on Frankford Arsenal technical report AD0223114.

EPP9	%	gr
K Picrate	22.5	7.4
Pb(NO ₃) ₂	28.0	9.2
Ba(NO ₃) ₂	25.5	8.4
CaSi ₂	11.0	3.6
PbO ₂	5.0	1.7
Sb ₂ S ₃	5.0	1.7
Tetracene	3.0	1.0

An interesting aspect of this formula is that a double exchange reaction occurs when the compound is moistened with water. As the lead nitrate reacts with the potassium picrate to make Basic lead picrate, it also produces potassium nitrate which acts as an oxidizer along with the barium nitrate.

To make primers, combine the dry powders at the specified percentages given in the EPP9 formula and blend/mix them well in a non-porous mortar and pestle. It is safe to handle this dry mixture without fear of an explosion. Dry pack primer cups as normal and lightly compress the powder into a pellet. It should be noted that this mixture is extraordinarily clumpy and it was a challenge to cleanly fill the primer cups with loose powder. Next, completely moisten the pellet with a 50/50 blend of water/alcohol solution to initiate the lead picrate reaction. While still moist, complete the buildup of the primers with the addition of a paper foil and anvil. The completed primers are then allowed to dry; either 2-3 days at room temperature, or preferably for 2 hours at 45-50°C (113-122°F). The dried primers are only slightly less powerful than primers based on lead styphnate. They were found to work very well in test rounds. EPP9 primers seem to be unaffected by storage at normal household temperature and humidity for at least 6 months (max age on prepared primers).

For rimfire use, a mixed technology primer was found to be best to provide a durable primer pellet yet powerful firing. The following formulas combine basic lead picrate and lead nitratohypophosphite technologies.

As is typical in the Eley Prime method, approximately 20 mg of dry primer compound is placed into each case. Enough 50/50 water/alcohol solution is added to make a slurry. After mixing well and working the moist compound into the rim area, the case is allowed to sit until the pellet hardens (~2-5 minutes). It is then dried either at room temperature for 2 days, or at 50C for 1-2 hours.

Rimfire Formulation EPP 12

	%	gr
K Picrate	17.7	5.8
Pb(NO ₃) ₂	45.3	14.9
Pb(H ₂ PO ₂) ₂	12.0	4.0
Glass	25.0	8.3

A similar formula that makes more efficient use of the lead nitrate (i.e. amount is calculated to exactly what is needed to react with the potassium picrate and lead hypophosphite) is shown below.

Rimfire Formulation EPP 14

	%	gr
K Picrate	14.0	4.6
Pb(NO ₃) ₂	37.5	12.4
Pb(H ₂ PO ₂) ₂	20.0	6.6
Tetracene	3.5	1.2
Glass	25.0	8.3

This formula is more powerful than EPP12 and is similar to lead styphnate based rimfire primers like EPM4 and EPM11.

Primers made with Lead Picrate / Lead Nitrate / Lead Acetate Clathrate.

In 1966, Remington employee J. F. Kenney patented (US3293091) an interesting series of compounds called "clathrates" that were useful in primer and other igniter formulations. In his example #1, a combination of basic lead picrate, lead nitrate, and lead acetate gave a clathrate (LP/LN/LA) that was both powerful and static insensitive. This compound can be easily made at 1/10 scale using Kenney's laboratory method which yielded around 6 gm of compound. Kenney's other clathrate materials were not tried, but may give useful and powerful primer compounds (see patent for more information).

The preferred LP/LN/LA clathrate primer formulations for rimfire and centerfire use are shown below as EPM 7 and EPM 8:

US3293091

Rimfire Formulation EPM 7

	%	gr
LP/LN/LA	46.0	15.2
Ba(NO ₃) ₂	50.0	16.5
Tetracene	4.0	13

US3293091

Centerfire Formulation EPM 8

	%	gr
LP/LN/LA	42.0	13.9
Ba(NO ₃) ₂	44.0	14.5
CaSi ₂	7.0	1.3
Al	5.0	1.7
Tetracene	2.0	0.7

WARNING: These formulations are complete and ready to fire once mixed. Only produce and store ≤ 33 gr of compound at a time and use appropriate handling precautions.

Approximately 20 mg of the rimfire formula EPM 7 was placed into a prepared 22LR case and moistened with a dilute solution of shellac in ethanol. This solution both allows the compound to be more easily worked into the rim area as a paste and also acts as a binder upon drying. Unfortunately, adding enough shellac to the primer compound to make a durable pellet also killed the primer. Therefore a mixed technology primer was necessary to make a durable pellet and assure reliable firing. Just like with EPM 4 and EPP 12, a blend of 50% EPH 0 and 50% EPM 7 was made to create EPM 12.

50% EPH 0 / 50% EPM 7

Rimfire Formulation EPM 12

	%	gr
LP/LN/LA	23.0	7.6
Ba(NO ₃) ₂	25.0	8.3
Tetrazene	2.0	0.7
Pb(NO ₃) ₂	20.0	6.6
Pb(H ₂ PO ₂) ₂	20.0	6.6
Grit	10.0	3.3

This formula fired strongly but showed only a small amount of muzzle flash.

The centerfire formula, EPM 8, gives a powerful, clean burning primer that is among the strongest non-corrosive primers tested. While not necessary, moistening the compound with plain ethanol aided in seating the anvil in SP primers by allowing the compound to flow as the anvil is pressed into place.

Making Non-Toxic (aka Green) Primers

Although quite rare, a few people each year are exposed to enough lead vapors from the firing of ammunition that they suffer from symptoms caused by lead poisoning. People have been historically wary of lead for centuries because of the risks and effects of lead poisoning. In past centuries, lead in pewter plates and utensils was a serious problem that was solved by carefully defining and regulating the composition of pewter to make sure it was lead free. More recently, lead based paints have been discontinued due to problems with children eating paint chips that flaked off of home walls and being poisoned. Finally, good practices in the casting of lead bullets require that it be done in a well ventilated area to avoid excessive exposure to lead fumes. So, anytime there is a significant risk of exposure to lead and its compounds, one can expect the government to get involved to reduce or eliminate the risk through regulations and laws. This has already occurred in California which has banned lead shot in shotgun shells. Although non-lead primers are not yet required, the primer industry has been working on non-lead primers for several decades in anticipation of the eventual banning of lead in their formulations. These lead free primers are commonly referred to as non-toxic or green. In most cases, the Lead Styphnate (and/or Lead Azide) primary is replaced with an organic high energy compound. The most common are 1) Diazodinitrophenol or DDNP, 2) Potassium dinitro benzofuroxane or KDNBF, and 3) Tetrazene (as already presented in this document). One other approach being advanced by ATK (parent company of Federal, CCI, Blazer,...etc.) involves the use of red phosphorus. In fact, red phosphorus makes excellent ammunition primers and its use was well known as far back as the 1940s. However, shelf life was not very good since red phosphorus tended to react with the other primer ingredients or the metal primer cup eventually killing the primer. ATK has fixed this problem by coating the red phosphorus particles with various materials to isolate them from the other primer ingredients. Only time will tell which of these approaches, if any, will be commercially successful.

Primers made with DDNP.

Of the non-toxic primer formulations, those based on DDNP are the easiest to prepare. As with other non-corrosive formulations we have presented, some wet chemistry work is required to synthesize DDNP as it cannot be purchased. The starting material for making DDNP is picramic acid (2-amino-4,6-dinitrophenol). Regrettably, while picramic acid is commercially available it is expensive and difficult to purchase, so it is normally synthesized from picric acid (2,4,6-trinitrophenol). Picric acid is also commercially available, but is ~\$150/lb and also difficult to purchase, so it is typically synthesized from either phenol or aspirin. So, the synthesis chain is as follows:

Aspirin -> Picric Acid -> Picramic Acid -> DDNP

Synthesis methods for each step are presented below.

Picric Acid

This synthesis was covered in the previous section on making basic lead picrate primers.

Picramic Acid

$C_6H_3N_3O_7 + NaOH \rightarrow C_6H_2N_3O_7Na + H_2O$ (Picric acid neutralized to sodium picrate)

$S + NaOH \rightarrow Na_2S_x$ (Sodium Polysulfide)

$C_6H_2N_3O_7Na + \text{Reducing compound} \rightarrow C_6H_4N_3O_5Na$ (Sodium picrate reduced to sodium picramate)

<u>Materials</u>	<u>Equipment</u>
Picric Acid	2x 600ml Beakers
Sodium Hydroxide	Glass funnel
Sulfur	1000ml beaker
Sulfuric Acid	Ice bath and equipment
Sodium Nitrite	200ml evaporating dish
Acetone	250ml beaker

Into a 600ml beaker, pour 100mls of water and heat up to ~70-80C. Add 9 grams of finely powdered picric acid to this and swirl it a little bit. It will not all dissolve however, so don't assume you're getting anywhere by swirling it for 24 hours. Now add 1.5 grams of sodium hydroxide to this. Swirl this mixture around until everything inside dissolves. Yes it will all dissolve just keep swirling. The solution will turn to an orangish color. This is a sodium picrate solution. Keep this on low heat and add water as it evaporates. In another beaker, pour 300mls of water and 8.0 grams of sodium hydroxide. Bring the solution to a rolling boil. Measure out 7.5 grams of pure sulfur, and crush it finely. Seive it into the boiling sodium hydroxide solution making sure to get as little sulfur on the sides of the beaker as possible. Let this boil for 60-120min (1 to 2 hours), adding water as necessary. After this amount of time, most if not all of the sulfur should be dissolved. If you sit and watch it the whole time, you will notice a color change from clear to green to blue, to puke green, to pea green, then to a very dark color and once all the sulfur dissolves it will be a very dark red color. Set this on a towel or similar device and let it cool down until it stops boiling. The reason for the towel is so that it doesn't come in direct contact with any room temperature (or colder) surface. Once it stopped boiling (but is still hot) add it to the sodium picrate solution in the other beaker, in 4 portions. Once all of it is added, place the beaker in a refrigerator (about 4C) until its cold. There should be a healthy amount of red crystals in the bottom of the beaker. Filter the whole solution into the 600ml beaker that was used in the last step. Discard the filtrate and clean that beaker out. Pour 300mls of water in it and bring it to a boil. Add the red crystals in the filter (and everything else) to the boiling water and boil it for 2-3 minutes. While it is still boiling clean out the other 600ml beaker which should be empty. Filter the boiling solution into the clean 600ml beaker. Discard the filter and its contents and let the filtrate cool to room temp. This is now a sodium picramate solution.

DDNP

$C_6H_4N_3O_5Na + H_2SO_4 \rightarrow C_6H_5N_3O_5 + NaHSO_4$ (Sodium picramate acidified into picramic acid)

$C_6H_5N_3O_5 + HNO_2 \rightarrow C_6H_3N_4O_5$ (picramic acid diazotized)

When the sodium picramate solution from above is at room temp, drip concentrated sulfuric acid in with stirring. Keep dripping it in until it just barely tests acidic on litmus paper. This will take 1-2ml. You will also notice that the color has changed from a deep red color to a sort of rusty color. There is also a precipitate in the beaker (and a lot of it). This is picramic acid. Measure out 7.5 grams of sulfuric acid and add it to this beaker. Mix the beaker up, then pour it into a 1000ml beaker. Add another 100ml of water to this. Place this beaker in an ice bath and bring the temperature down below 5C. In another 600ml beaker, pour 250ml of water and add 5.4 grams of sodium nitrite. Swirl it until its dissolved. Now, slowly add this solution to the picramic acid solution in the 1000ml beaker, keeping the temperature below 5C. Be sure to stir almost constantly during this part. Once all of it is added, continue stirring for a couple more minutes then remove it from the ice bath. Let it slowly warm up to room temperature. You will see a brown precipitate (the shade of brown varies sometimes).

Once it is up to room temperature, filter the solution out. There are a lot of DDNP crystals in here, so use two different filter papers. Try to even the amounts of DDNP on each filter paper when filtering. Once all the crystals are filtered out, run 60ml of cold water through each filter to wash out some of the very soluble products. Remember, DDNP is slightly soluble in water so make sure its cold. Scrape the DDNP on the filter papers into a 250ml beaker. Add acetone to this, 100-150mls should be fine to dissolve all the DDNP. Swirl it around good to dissolve as much as possible. There will be a significant amount of impurities that are undissolved which should be yellow; the solution should be brown. Filter this solution out into a 200ml evaporating dish. Discard the filter and its contents. Place the 200ml evaporating dish on top of a 1000ml beaker with boiling water in the bottom of it. Keep boiling the water so that the steam boils away the acetone (do this outside or with good ventilation). Eventually you will be left with a brown crystal in your evaporating dish. This is pure DDNP. DO NOT SCRAPE THIS STUFF OFF THE EVAP DISH. Get as much as you can of the loose crystal, but don't scrape at the layer stuck to the evaporating dish because this compound is friction sensitive.

Once the DDNP has been synthesized it is used as follows in a centerfire primer formula.

EPN 0

	%	gr
DDNP	17.0	5.6
Ba(NO ₃) ₂	34.0	11.2
Sb ₂ S ₃	24.0	7.9
CaSi ₂	10.0	3.3
PbO ₂	10.0	3.3
Tetracene	5.0	1.7

The new "green" primer formulations present a major challenge to forensic chemists since the heavy metal signature from normal primers is no longer present. Without these heavy metals, it becomes very difficult to determine the distance between the gun and a gunshot victim. It is even difficult to pickup

any evidence that a shot was fired when the suspected shooter's hand is swabbed. Much work is currently being done to solve these analytical problems when green ammunition is used in a crime.

Appendix

References

Ammunition Making – An Insider’s Story, George E. Frost, NRA, 1994

Poor Man's Primer Manual, George B. Dmitrieff, Desert Publications, 2001

Explosives Engineering, Paul W. Cooper, Wiley-VCH, 1996

Priming Compounds, Bev Fitchett’s Guns Magazine, <http://www.bevfitchett.com/chemical-analysis-of-firearms/priming-compositions.html>

Hatcher’s Notebook, Julian S. Hatcher, The Military Services Publication Company, 1947

Improvised Primary Explosives, Dirk Goldman, Internet, 1998

Manual of Explosives, Military Pyrotechnics, and Chemical Warfare Agents, Jules Bebie PhD, MacMillan, 1943

Ordnance and Gunnery, Ormond Michell Lissak, John Wiley and Sons, 1908

Primer mixes composition and behavior, Marco Morin PhD, 2008,
http://www.academia.edu/3157491/Primer_mixes_composition_and_behaviour

Improvised Munitions Handbook, TM 31-210, Department of the Army, 1969

....plus too many patents to mention

Primer chemical suppliers

There are a large number of online chemical suppliers for the closely related fireworks hobby. They carry almost everything you will need. Prices and shipping charges vary widely, so comparison shop before buying. Also, most of these suppliers require that oxidizers (e.g. potassium chlorate) and fuels (e.g. antimony sulfide and sulfur) be shipped (and sometimes even ordered) separately which increases the shipping costs. The more general laboratory suppliers, like CitiChemical and Elemental Scientific also carry glassware and other laboratory equipment that may prove useful. Also, be sure to checkout Amazon and eBay as they carry a surprising number of chemicals and laboratory equipment. The author has purchased chemicals from Hobby CS, Pastime, Firefox Pyrotechnic, PyroChemSource, Amazon, and eBay. Note that some companies will require a copy of your driver’s license and a signed liability release before they will sell to you. One should assume that this information will eventually find its way to various governmental agencies.

Skylighter <http://www.skylighter.com/mall/chemicals.asp>

Hobby CS	http://www.hobbychemicalsupply.com/servlet/StoreFront
Thunder	http://www.highqualitychems.com/servlet/StoreFront
PyroChemSource	http://www.pyrochemsource.com/Chemicals-Chemicals-AL/b/4940415011
FireChemical	http://www.firechemical.com/
Pastime	http://pastimepyrochemicals.com/
American Pyro	http://www.americanpyrosupply.com/Products-PYROTECHNIC_CHEMICALS.html
CitiChemical	http://www.chemsavers.com/
Elemental Scientific	http://www.elementalscientific.net/store/scripts/default.asp
Firefox Pyrotechnic Chemicals	http://www.firefox-fx.com/index.htm
Amazon	http://www.amazon.com
eBay	http://www.ebay.com
Ace Hardware	for shellac and denatured ethyl alcohol, also available from Lowes, Home Depot

Primer formulations

H-48 Primer Compound

Potassium chlorate	51.5%
Antimony sulfide	27.3%
Sulfur	9.1%
Glass powder	12.1%
Sodium Bicarbonate	trace (optional)
Aluminum powder	trace (optional)

H-42 Primer Compound (used for almost all WW1 military ammunition)

Potassium chlorate	47.2%
Antimony sulfide	30.83%
Sulfur	21.97%

This formulation removes the ground glass used in H-48 that was suspected of causing excessive barrel wear. This is an unproven suspicion and probably not true because of the fineness of the ground glass (more likely to act as a polishing agent than an abrasive.)

FA-70 (used from 1917 until mid-1950's by the US military)

Potassium chlorate	53.0%
Lead Thiocyanate	25.0%
Antimony sulfide	17.0%
TNT	5.0%

Note: a finely ground fast pistol powder can replace the TNT in this formulation.

Lead Thiocyanate is a restricted (and expensive, \$45/lb) chemical and must be synthesized to make this formulation. This primer mixture has better storage life than H-48 or H-42 compounds because of the replacement of sulfur by lead thiocyanate.

EPH 0 (Rimfire Formulation)

	%	grains
Pb(H ₂ PO ₂) ₂	40.0	13.2
Pb(NO ₃) ₂	40.0	13.2
Glass	20.0	6.6

EPH 10 (Centerfire Formulation)

	%	grains
Pb(H ₂ PO ₂) ₂	20.0	6.6
Pb(NO ₃) ₂	20.0	6.6
Ba(NO ₃) ₂	39.0	12.9
CaSi ₂	11.0	3.6
PbO ₂	5.0	1.7
Sb ₂ S ₃	5.0	1.7

EPT 3 (Centerfire Formulation)

	%	gr
Tetrazene	40.0	13.2
Ba(NO ₃) ₂	32.0	10.6
Sb ₂ S ₃	20.0	6.6
CaSi ₂	8.0	2.6

EPS 5 (Centerfire Formulation)

	%	gr
Styphnic Acid	20.0	6.6
PbO	18.0	5.9
Ba(NO ₃) ₂	39.0	12.9
CaSi ₂	11.0	3.6
PbO ₂	5.0	1.7
Sb ₂ S ₃	5.0	1.7
Tetrazene	2.0	0.7

EPS 0 (Rimfire Formulation)

	%	gr
Styphnic Acid	21.6	7.1
PbO	19.9	6.6
Ba(NO ₃) ₂	20.0	6.6
Tetrazene	3.5	1.2
Glass	35.0	11.6

EPS 2 (Rimfire Formulation)

	%	gr
Styphnic Acid	24.9	8.2
PbO	23.0	7.6
Ba(NO ₃) ₂	22.5	7.4
Tetrazene	4.6	1.5
Glass	25.0	8.3

50%EPH0/50%EPS0**EPM 4 (Rimfire Formulation)**

	%	gr
Styphnic Acid	10.8	3.6
PbO	10.0	3.3
Ba(NO ₃) ₂	10.0	3.3
Pb(H ₂ PO ₂) ₂	20.0	6.6
Pb(NO ₃) ₂	20.0	6.6
Tetracene	1.8	0.6
Glass	27.5	9.1

EPM 11 (Rimfire Formulation)

	%	gr
Styphnic Acid	10.8	3.6
PbO	10.0	3.3
Ba(NO ₃) ₂	10.7	3.5
Pb(H ₂ PO ₂) ₂	20.0	6.6
Pb(NO ₃) ₂	20.0	6.6
Tetracene	3.5	1.2
Glass	25.0	8.3

EPP 9 (Centerfire Formulation)

	%	gr
K Picrate	22.5	7.4
Pb(NO ₃) ₂	28.0	9.2
Ba(NO ₃) ₂	25.5	8.4
CaSi ₂	11.0	3.6

PbO2	5.0	1.7
Sb2S3	5.0	1.7
Tetracene	3.0	1.0

EPP 12 (Rimfire Formulation)

	%	gr
K Picrate	17.7	5.8
Pb(NO3)2	45.3	14.9
Pb(H2PO2)2	12.0	4.0
Glass	25.0	8.3

EPP 14 (Rimfire Formulation)

	%	gr
K Picrate	14.0	4.6
Pb(NO3)2	37.5	12.4
Pb(H2PO2)2	20.0	6.6
Tetracene	3.5	1.2
Glass	25.0	8.3

EPM 7 (Rimfire Formulation)

	%	gr
LP/LN/LA	46.0	15.2
Ba(NO3)2	50.0	16.5
Tetrazene	4.0	1.3

EPM 8 (Centerfire Formulation)

	%	gr
LP/LN/LA	42.0	13.9
Ba(NO3)2	44.0	14.5
CaSi2	7.0	2.3
Al	5.0	1.7
Tetrazene	2.0	0.7

EPN 0 (centerfire formula)

	%	gr
DDNP	17.0	5.6
Ba(NO3)2	34.0	11.2
Sb2S3	24.0	7.9
CaSi2	10.0	3.3
PbO2	10.0	3.3
Tetracene	5.0	1.7

Synthesis of primer chemicals

This is a high level subject that will be left for an advanced course. However, if you are interested, the Internet can provide you with the information you need to make almost any primer chemical. Patents are especially useful and easily accessible. Do not be surprised if many excellent synthesis methods were developed in the first half of the twentieth century. Just because it is old does not mean it is obsolete.

For example, it is surprisingly easy to synthesize potassium chlorate from ordinary household bleach and salt substitute (potassium chloride). You can also make potassium chlorate electrochemically directly from salt substitute. Various lead salts can be made starting with lead fishing weights and certain acids. It is impossible for government authorities to restrict every possible compound that can be used to make primer chemicals. However, with control of the Internet, they can make it difficult to learn how to convert these common materials into useful chemicals. So, now is the time to learn and share what you know with as many people as possible. Indeed that is one of the primary purposes of this course.

Revision History

Date	Revision
April 29, 2014	Original issue
January 6, 2016	Update with added formulations for Non-Mercuric/Non-Corrosive Primers and general editing to improve clarity, spelling, and grammar in all sections
February 29, 2016	Added page numbers and completed the section on green primers
September 4, 2017	Added section on non-corrosive Picric Acid based primers and LP/LN/LA clathrate based primers