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AMMUNITION MANUFACTURE

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6 Claims. (Cl. 117—89)

This invention relates to the manufacture of metallic components of ammunition from corrodible metals, such as ferrous metals, and particularly to the protection of such articles from corrosion and rusting under conditions of storage and use.

Metallic components of firearms ammunition, such as cartridge cases, primer cups, shot shell heads and battery cups, are ordinarily made by striking cup-shaped blanks from a flat sheet and subsequently reforming the cups in a series of suitable drawing, or alternate drawing and annealing, operations to the desired finished form. Since ammunition including such components may be in storage for substantial periods of time under a wide variety of storage conditions, it is essential that the metal be immune to atmospheric corrosion. For this reason, metallic ammunition components are almost universally made of non-corrodible metals, such as copper, gilding metal, or brass containing a relatively high percentage of copper. Efforts have been made to utilize plated ferrous metals for this purpose, but these efforts have been unsuccessful. Electrolytic platings of copper, nickel, zinc and the like are known to be porous in character and ineffective as protecting media unless the plating is of excessive and undesirable thickness. Such rust preventives as "Parkerizing" are ineffective for similar reasons. Considering for example, the manufacture of metal shot shell heads, the blank which is cut from sheet is drawn, annealed, re-drawn and trimmed to a configuration approaching its finished shape, and in this condition is assembled with a paper body and a base wad. The assembly is then subjected to a high pressure, which materially deforms both the base wad and the metal head, securing both to the paper body. The die friction and deformation stresses in this operation tend to break the continuity of any rust preventive coating which may have been previously applied, and subsequent rust preventive treatment is impracticable, due to the fact that the metal has been assembled with non-metallic components.

The present invention comprises the discovery of methods and materials by which ammunition components of ferrous metals can be adequately and satisfactorily protected against corrosion. The method is preferably, but not necessarily, practiced in conjunction with electrolytic plating; that is, the sheet or strip, or the partially or fully formed components made therefrom, is first given a thin plating of a relatively non-corrodible metal, such as copper, nickel or zinc. This plating in itself, as heretofore explained, does not furnish the desired measure of protection, on account of its notoriously porous character. The hydrophylic character of the ferrous metal, in conjunction with electrolytic action of copper and nickel, tends to accelerate corrosion of the surfaces of the ferrous metals which are exposed due to the discontinuity of the plating. It therefore becomes desirable to treat the plated surface with a passivating agent having such an affinity for the ferrous metal as will render it hydrophobic and oleophylic. For best results, there is also applied to the surface a water-repellant corrosion-resistant material of an oleagineous character, the intermediate material furnishing a bond between the metal itself and the water-repellent corrosion-inhibiting coating and likewise preventing tarnish of the plate. The intermediate is preferably an acid group having a strong attraction for metals. The corrosion inhibitor is preferably an aliphatic monoamine comprising one chain of at least six carbon atoms, or a derivative of such an amine, or a mixture of such an amine or amine derivative, with a wax; in the case of secondary and tertiary amines one chain only need comply with this description.

Specific examples of the practice of the invention are as follows:

Example I

Cold rolled steel strip of 0.015'' thickness is punched and cupped, then plated electrolytically with 0.0004'' of bright copper. The plated cups are converted by known steps to shot-shell heads ready for assembly with paper bodies, and these heads basket-dipped in an aqueous solution comprising 0.5% CrO_3 and 0.01% fatty alcohol sulphate. After five minutes' immersion the heads are removed from the CrO_3 solution and dried by tumbling in a blast of heated air. The heads are next dipped briefly in a hot (60° C.) solution of 4% of a technical mixture of alkyl amines corresponding to the alkyl alcohols obtained by catalytic hydrogenation of coconut oil acids and 6% paraffin wax (melting point 57° C.) in a 1/1 mixture of acetone and toluene. On removal from this solution the heads are tumbled to rid them of excess solution and dried in a blast of hot air for two to three minutes.

Example II

Steel strip is hot rolled to 0.055'' thickness and plated on one side with 0.0041'' of bright copper. The plated strip is then cold rolled to 0.015'' thickness and shot shell heads fabricated from this composite sheet in the usual manner with

the copper side out. These heads are dipped in bulk in a solution comprising 2% CrO_3 in a 4/1 mixture of acetone and water, removed after five minutes' immersion, rinsed with cold water and dried by tumbling in warm sawdust. The heads are next dipped briefly in a hot (60° C.) solution of 4% of a technical mixture of alkyl amines corresponding to the alkyl alcohols obtained by catalytic hydrogenation of sperm oil and 6% beeswax in 1/1 acetone/toluene, drained and tumbled to remove excess solution, and finally dried in hot air at a temperature of about 90° C.

Example III

Copper-plated shot shell heads are fabricated as described in Example I up to the point of dipping in an aqueous solution of CrO_3. At this stage the heads are boiled for ten minutes in a 4% aqueous solution of n-dodecyl ammonium dihydrogen phosphate, drained and dried in a current of air at room temperature. The heads are then dipped in a hot (60° C.) solution of 5% carnauba wax in V. M. & P. naphtha, drained and dried by tumbling in a current of warm air.

Example IV

Hot rolled steel sheet of 1/8" thickness is blanked, cupped and converted into .38 caliber cartridge cases by known methods. These cases are plated with 0.0003" of bright nickel and then immersed for fifteen minutes at room temperature in an aqueous solution comprising 4% H_3PO_4 and 0.05% fatty alcohol sulfate. The cases are then rinsed with cold water, dried and finally treated with an amine wax mixture as in Example II.

Example V

Rim fire cartridge cases (.22 caliber) are formed from 0.024" cold rolled steel strip by well known steps and plated with 0.004" bright zinc. The cases are then dipped briefly in a 4% solution of n-dodecyl ammonium acid chromate in 9/1 toluene/acetone at room temperature, drained and dried in a current of air. This treatment is followed by brief immersion in a hot (60° C.) solution of 6% Asiatic paraffin wax in petroleum distillate, after which the cases are tumbled to remove excess solution and dried in a current of warm air.

Example VI

Copper-plated shot shell heads are fabricated as described in Example II up to the point of dipping in aqueous CrO_3 solution. These heads are then immersed for ten minutes in a solution of 4% n-dodecyl acid phthalate and 6% beeswax in acetone/toluene maintained at 50° C. After removal the heads are tumbled and dried in hot air.

Example VII

Shot shell heads fabricated from steel, and plated with bright zinc in the manner described in Example V, are treated first with aqueous CrO_3 solution and then with amine-wax solution as described in Example I.

Example VIII

Copper-plated shot shell heads are prepared according to the method described in Example I up to the point of dipping in aqueous CrO_3 solution. These heads are then immersed for five minutes at room temperature in a solution of 5% H_3PO_4 and 0.5% $NaNO_3$ in water, rinsed well with hot water and finally with a 5% solution of $NaNO_2$ in water. After drying in a current of hot air the heads are treated with amine-wax solution as described in Example II.

Example IX

Copper-plated steel shot shell heads prepared for assembly as described in Example I are given a pre-treatment comprising immersion for one minute in a boiling aqueous solution of 10% phosphoric acid and 1% sulphuric acid, rinsed in water at room temperature, dried in a current of warm air or in sawdust, then treated with a solution of 2% to 4% of an amine or amine derivative and about 6% wax in petroleum distillate (commercial "Shell Sol") at room temperature, and dried in a current of warm air.

Example X

The procedure is similar to Example IX except that the pre-treatment consists of immersion for about thirty seconds in a boiling aqueous solution of 2% sulphuric acid.

Example XI

The procedure is similar to Example IX except that the pre-treatment consists of immersion for about one minute in a boiling aqueous solution of 4% phosphoric acid and 1% sulphuric acid.

Example XII

The procedure is similar to Example IX except that the pre-treatment consists of immersion for about two minutes in a boiling aqueous solution of 3% phosphoric acid.

Example XIII

The procedure is similar to Example IX except that the pre-treatment consists of immersion for about two minutes in a cold aqueous solution of 2% chromic acid.

Example XIV

The procedure is similar to Example IX except that the pre-treatment consists of immersion for about two minutes in a cold aqueous solution of 1% chromic acid and 0.5% sulphuric acid.

Example XV

Plated steel shot shell heads, prepared for assembly as described in Example I, either with or without the pre-treatment described in any of the foregoing examples, are treated with a solution of about 10% of commercial "Alox" and 2% to 4% of dodecyl ammonium acid chromate or dodecyl ammonium chromate in toluene or other organic solvent, and dried in a current of warm air.

Example XVI

Plated steel shot shell heads, prepared for assembly as described in Example I, are treated with a solution in toluene or other suitable organic solvent of a suitable wax and an amine or amine derivative.

Example XVII

Cups for the production of rimfire shells are struck from steel strip, plate, processed by appropriate drawing and annealing operations to finished condition, subjected to a pretreatment in accordance with any of the foregoing examples, then primed and loaded. The finished cartridges are then tumbled in sawdust, scrap felt or similar distributing medium, containing 5% to 15% by volume of paraffin oil and 2% to 4% by volume of a suitable amine or amine derivative, such as dodecyl amine.

Example XVIII

Plated steel shot shell heads prepared for assembly as described in Example I are subjected, for a time depending upon the temperature used, to a temperature adequate to produce a protective oxide film. Typical conditions are exposure to a temperature of 150° F. for 8 minutes; at lower temperatures a longer exposure is necessary, and at higher temperatures a shorter exposure is adequate. The articles are then subjected to a wax-amine treatment in accordance with Example IX.

It will be understood that drying after pretreatment may, if desired, be performed at relatively high temperatures, and that drying after the application of the wax-amine coating must be performed at a temperature sufficiently high to prevent crystallization of the wax in a noncontinuous film.

Shot shell heads treated in accordance with the foregoing examples are then assembled with paper body and base wad, to which they are secured by a relatively severe "heading" operation, as heretofore described. They are then primed and loaded in the usual manner, and subjected to the following corrosion tests:

1. Salt spray—3% solution, continuous test for 48 hours.
2. Humidity oven—temperature 120° F., relative humidity 90%, continuous test for 2 to 3 months.
3. Outdoor exposure—continuous test for 2 to 3 months on roof unprotected from sun or rain.
4. Exposure to hydrogen sulphide atmosphere for a time sufficient to tarnish ordinary brass heads.

In the foregoing tests of steel shot shell heads, ordinary brass heads, as well as plated but untreated steel heads, were exposed along with the heads under test, for the purpose of comparison. The brass heads all showed tarnish and dezincification, and the plated but untreated heads showed substantial rusting; while the heads treated in accordance with the examples showed no material tarnish or rust.

As heretofore indicated, the reagent utilized in the initial treatment may be any acid group having a high degree of attraction for the metal, such as chromic, phosphoric, molybdic or sulphuric acids or mixtures thereof, and salts, of which ferrous dihydrogen phosphate, manganous dihydrogen phosphate, zinc dihydrogen phosphate, potassium dichromate, and sodium dimolybdate, may be taken as typical.

Copper is preferred as a plating or coating material for the ferrous metal base in small arms ammunition components. Other relatively noncorrodible metals which may be used include nickel, zinc, cadmium, chromium, tin and alloys such as brass and the product used in making terne plate. These metals may be applied by any suitable means to finished parts, as for example by electroplating, dipping, ionic displacement, spraying, sherardizing, or distillation and condensation. If the surface metal can be drawn, as in the case of copper, brass and zinc, it may be applied to the original sheet from which the parts are formed or at any subsequent point in the fabrication. When applied to the finished parts a thickness of 0.0004"–0.0010" is preferred, although a coating of 0.0001"–0.0050" can give the desired results. If applied prior to this point, the thickness used should be adjusted to yield the proper value in the finished article.

When using chromic acid, acid chromates, or molybdic acid, the reagent may be dissolved in water alone, but to secure better wetting it is customary to add small percentages of wetting agents or varying amounts of water miscible organic liquids. Among the suitable water miscible organic liquids are ketones such as acetone, ethers such as dioxan, and alcohols like methanol and ethanol. These may be added to water in proportions varying from 10% to 90%, although the range of 50% to 80% is preferred. Unless the acid solution is removed by rinsing it is best to use liquids boiling under 150° C., so that evaporation will not be retarded. In many cases the use of wetting agents presents certain advantages, so that solutions are often employed which contain between 0.005% and 1%, and usually between 0.01% and 0.1%, of such compounds as long chain fatty alcohol sulfates, sulfonated naphthalene derivatives, sulfonated castor oil and the like. The active component of these solutions, i. e., the chromic acid or its equivalent, can be present in concentrations ranging from 0.1% to 10%, and ordinarily is employed with the limits of 0.5%–5.0%. A wide range of temperatures is suitable for the treatment, so that although a temperature of 10°–40° C. is usually preferred, it is possible to obtain satisfactory results up to the boiling point of the solution. The time required for treating the metal parts will vary, depending on the concentration and temperature, and may range from the shortest possible dip to immersion periods of one hour or more. Conditions are usually adjusted so that the treatment may be carried out in ½–15 minutes. Agitation is desirable.

When using phosphoric acid or water soluble acid phosphates, the operation conditions and limits are quite similar to those outlined above except that higher concentrations are preferred and small proportions of accelerators are employed for their depolarizing action. Concentrations of the acid component usually range from 3% to 20% and may be varied within the limits of 0.5–35%. Accelerators are selected for their oxidizing action, and the soluble nitrates, nitrites, permanganates, chromates and dichromates, have been found suitable for the purpose. The concentration of these compounds usually is less than 1%.

Following the acid type treatment discussed above, ammunition parts are dried in preparation for the amine-wax treatment. When using phosphoric acid or its salts the parts should be rinsed well with hot or cold water. Such rinsing is optional with the other acid treatments, but is often used since it tends to prevent the discoloration sometimes obtained when conditions are not properly controlled. Drying may be accomplished by tumbling in hot air, or in some hot absorptive material such as sawdust, cotton waste and the like. Sufficient time should be allowed to permit essentially complete removal of all adhering moisture.

The corrosion inhibitor comprises an amine or derivative of an amine selected from the class of acyclic aliphatic monoamines having one aliphatic chain of at least six carbon atoms. The mixtures of amines indicated in certain of the examples are desirable by reason of their availability and relatively low cost. Decyl, hexadecyl, octadecyl and octadecenyl, and other long chain amines used alone are equally effective. In gen-

eral, those amines having an aliphatic group of ten to twenty-four carbon atoms, and especially those having an aliphatic group of twelve to twenty carbon atoms, are preferred. Suitable amine derivatives include the ortho phosphates of aliphatic monoamines having a chain of at least six carbon atoms, substituted ammonium chromates prepared from chromic acid and long chain aliphatic amines, and long chain alkyl ammonium metallo nitrites such as dodecyl ammonium cobaltinitrite ($(C_{12}H_{25}NH_3)_3Co(NO_2)_6$), dodecyl ammonium lead heptanitrite

$$((C_{12}H_{25}NH_3)_3Pb_2(NO_2)_7)$$

and similar compounds.

The wax may be an animal, vegetable or mineral product, and preferably should have a melting point above 40° C. Suitable waxes include carnauba, paraffin, ozokerite, Montan, myrtle, Chinese insect, Japan, spermaceti and beeswax. The solvent should be reasonably low boiling, preferably below 150° C., and a number of aromatic and aliphatic hydrocarbons are suitable for the purpose. When the amine-wax mixture follows a previous treatment with chromic acid, the solvent used should not dissolve this compound readily. Because of this requirement the alcohols, ketones and ethers are less satisfactory than the various naphthas and petroleum fractions which fall in the proper boiling range.

The solution of amine and wax may contain from 1% to 25% of each ingredient, and the proportions need not follow any particular ratio. Under most conditions it has been found that 2% to 10% of wax and a similar content of amine combine optimum ease of handling and protective value. The time of this phase of the treatment is not critical, and a brief dip ordinarily is sufficient. The temperature must be high enough to give a solution of good fluidity, and will usually be determined by the solubility characteristics of the wax, since the amines are quite soluble and may be used at any convenient temperature.

The indicated processes may be performed in the three separate steps of plating, applying the intermediate, and applying the water repellent; or, the second and third steps may be replaced by a single treatment, using a composition containing both the water repellent and the acidic anchoring groups.

The foregoing description is directed chiefly to a process comprising the three separate steps of plating, treating with an acid group, and treating with a corrosion inhibitor; however, as shown by some of the examples and elsewhere, some of these steps may be omitted or combined with others. Thus agents for combining the second and third steps are obtained by reacting the compounds used separately above, as for example the acid chromates and acid phosphate of long chain amines. In the case of acid phosphates the dihydrogen compound is preferred, as illustrated in Example III. Other long chain alkyl ammonium dihydrogen phosphates may be used, such as the heptadecyl, octadecyl and octadecenyl compounds, and the analogous acid chromates are similarly effective. Operative compounds are not limited to those containing an acidic group derived from an inorganic acid, for good results have been obtained with the n-dodecyl acid phthalate of Example VI and other acid esters of long chain alcohols and polycarboxylic acids. Dodecyl acid maleate and octadecyl acid maleate are other examples of this class.

It appears that the requisite corrosion resistance is secured from aliphatic carbon chains of at least six carbon atoms, and this limitation runs through both the stepwise and single stage treatments. Acidic anchoring linkages are obtained preferably from the inorganic acids mentioned previously when stepwise treatment is used, and from both these acids and organic acids for single stage treatments. When using preformed acidic compounds, the operating limits correspond closely to those outlined for a stepwise treatment; organic solvents are suitable for all agents while water can be used as a solvent only for the acid phosphates, concentrations may vary within the limits of 1–25% with 2–10% the preferred range, temperature must be sufficient to insure solutions of good fluidity, time of treatment may vary from a brief dip to immersion periods of one-half hour or more, and drying is carried out under the same conditions as described previously. Waxes may be combined with certain of these treatments or used subsequently to secure improved water repellence and mechanical resistance; in the case of acid chromates it is desirable that the wax treatment follow separately because of the degrading action of these reagents on other organic compounds.

A further variation in the described process (see Example XVII) contemplates the plating of ammunition components at an early stage in their production, say immediately after cupping, and the working of the plating in subsequent drawing operations to improve its character and continuity. The finished shell is treated with a suitable acid group, then primed and loaded, after which an oleaginous material, preferably paraffin oil in admixture with an amine as described is applied from a vehicle such as sawdust or scrap felt.

A further variation in the described process (see Example XVIII) contemplates treatment of the plated article by other means than the passivating and bonding agent. It has been found that maintaining the article at a suitable elevated temperature for an appropriate time, for example, a temperature of the order of 150° F. for an interval of about eight minutes obviates the necessity for treatment with an acid group.

The indicated variations and modifications of materials and procedure all come within the purview of the invention, which is limited only by a broad construction of the appended claims.

What is claimed is:

1. The method of manufacturing corrodible metal ammunition components comprising the steps of copper plating the component; subjecting the plated component to a solution containing an acid selected from the group consisting of phosphoric, sulphuric, chromic and molybdic acids; and then affixing a coating to the plated and passivated component comprising applying a composition thereto including wax and an aliphatic monoamine having at least six carbon atoms in one aliphatic chain.

2. The method of manufacturing cup-like corrodible metal ammunition components comprising the steps of copper plating the component; treating the component thus plated with a solution containing a passivating agent selected from the group consisting of chromic, moblybdic, phosphoric and sulphuric acids; and affixing a coating to the plated and passivated component comprising applying thereto a composition including wax and an aliphatic monoamine having at least six carbon atoms in one aliphatic chain and then performing further deforming operations on the component.

3. The method of manufacturing cup-like corrodible metal ammunition components comprising the steps of copper plating the component; treating the component thus plated with a solution containing a passivating agent selected from the group consisting of chromic, molybdic, phosphoric and sulphuric acids; and applying a coating by subjecting the plated and passivated component to a composition comprising a wax and dodecylamine.

4. The method of manufacturing shot shells having a paper body, base wad and corrodible metal head, comprising the steps of copper plating the metal head; treating the head with a passivating agent selected from the group consisting of chromic, molybdic, phosphoric and sulphuric acids; affixing a coating to the passivated head by subjecting the same to a composition comprising a wax and dodecylamine; and then assembling the body, base wad and head by a heading operation.

5. The method of manufacturing shot shells having a paper body, base wad and corrodible metal head, comprising the steps of copper plating the metal head; treating the head with a passivating agent selected from the group consisting of phosphoric, sulphuric, chromic and molybdic acids associated with a wetting agent; rinsing and drying the passivated heads; affixing a water repellant coating to the plated and passivated head by tumbling in sawdust impregnated with a composition of paraffin wax and dodecylamine; and then assembling the head, base wad and paper body by a heading operation wherein the head is deformed.

6. A corrodible metal ammunition component having a plating selected from the group consisting of copper, nickel, zinc, cadmium, chromium, tin and brass and a coating of a water repellant composition of wax and an aliphatic monoamine having at least six carbon atoms in one aliphatic chain, said coating being affixed to the plated article by an acidic compound resulting from the treatment of the plated article by a passivating agent selected from the group consisting of chromic, molybdic, phosphoric, sulphuric acids and their acidic salts.

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CERTIFICATE OF CORRECTION.

Patent No. 2,327,885. August 24, 1943.

ROBERT H. GRACE, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 40, Example V, for "0.004''" read --0.0004''--; and second column, line 66, Example XVII, for "plate" read --plated--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of November, A. D. 1943.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)

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(Seal) Acting Commissioner of Patents.