June 6, 1944. B. F. BUTLER ET AL 2,350,491

METAL DRAWING PROCESS

Filed Sept. 29, 1943 2 Sheets-Sheet 1

Fig. 1 Fig. 2 Fig. 3 Fig. 4 Fig. 5 Fig. 6

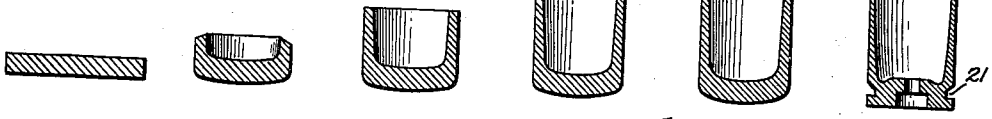


Fig. 7

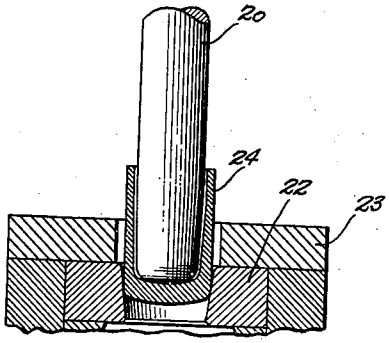


Fig. 8

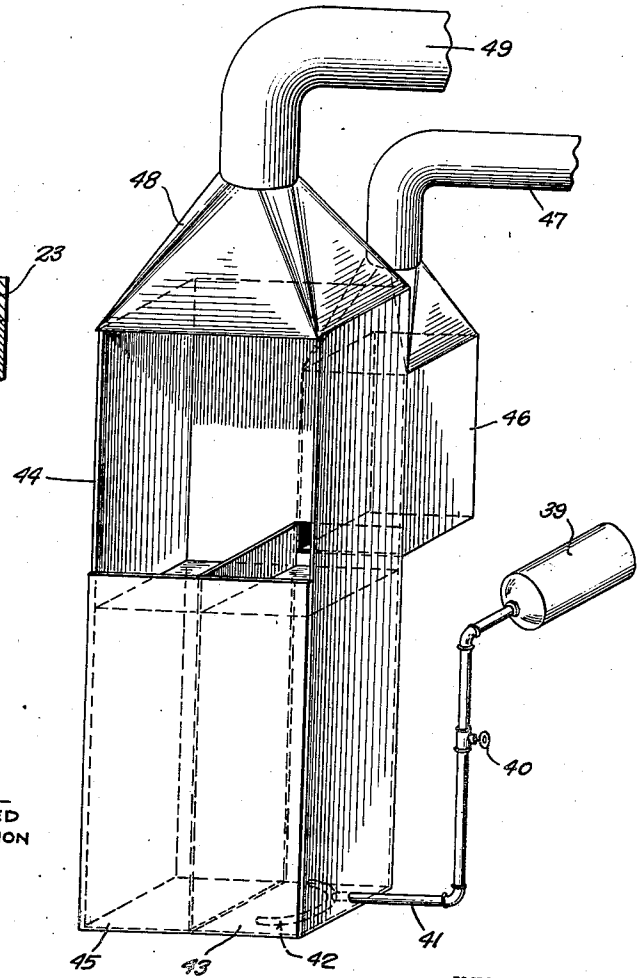
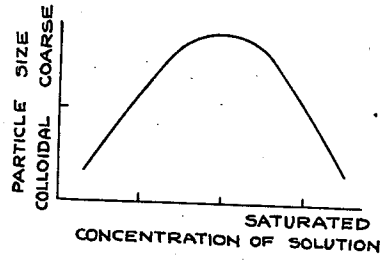


Fig. 11



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METAL DRAWING PROCESS

Filed Sept. 29, 1943 2 Sheets-Sheet 2

Fig. 9

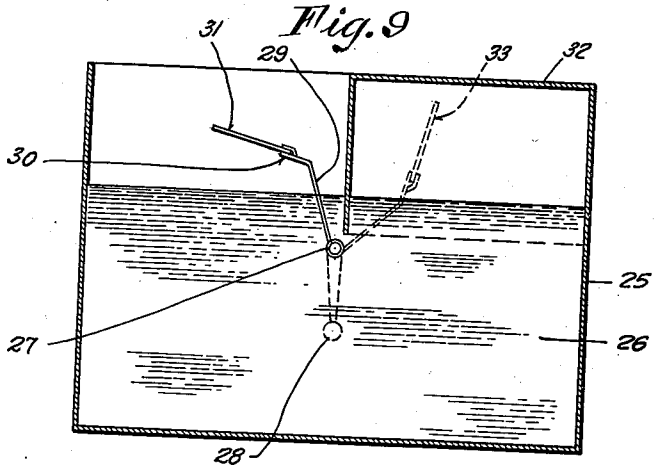
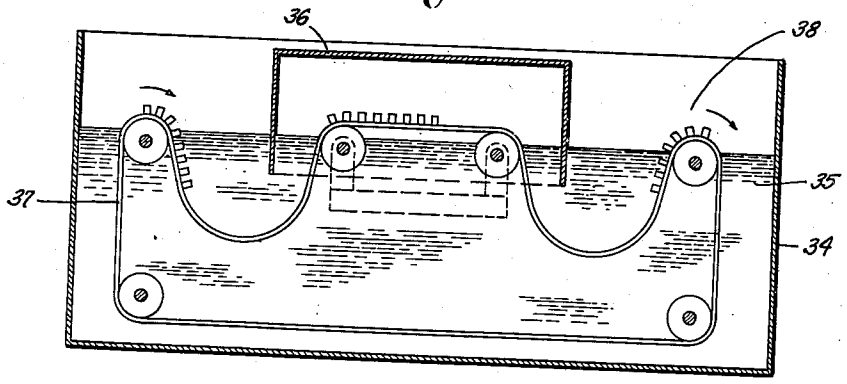


Fig. 10



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Patented June 6, 1944

2,350,491

UNITED STATES PATENT OFFICE

2,350,491

METAL DRAWING PROCESS

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Application September 29, 1943, Serial No. 504,254

17 Claims. (Cl. 205—8)

This invention relates to the manufacture of ferrous metal articles by mechanical working or plastic deformation, such as drawing, and is particularly applicable to shaping when the temperature of working is relatively low. One important use of the invention is in the drawing of steel cartridge cases or ammunition components.

In the manufacture of ammunition components, and especially cartridge cases, the surface must be free from imperfections such as scratches, because these imperfections are potential points of failure in the finished shell. The cartridge case is subjected to extremely high pressures upon firing and may be as high as 50,000 pounds per square inch in the conventional caliber .30 cartridge. The life of the drawing die is also an important factor in the quantity production of ammunition. A drawing aid must be provided which will give long die life and as near perfect surfaces on the drawn article as possible. The size of the case is critical so that if the die wears rapidly, it will be necessary to frequently change dies so as to maintain the correct dimensions. The characteristics of brass usually employed in the manufacture of cartridge cases are such that the metal will draw properly with a conventional lubricant but this is not so with steel.

In the present invention a process and drawing aid is employed which makes use of the reaction product of hydrogen sulphide in contact with iron. These and other objects of the invention will become apparent from the following description and the drawings.

In the drawings:

Fig. 1 represents a disc.

Fig. 2 represents a cup made from the disc.

Fig. 3 represents the cup of Fig. 2 after it has been passed through a drawing die.

Fig. 4 represents the cup of Fig. 3 after it has been passed through another die.

Fig. 5 represents the cup of Fig. 4 after it has been passed through a third drawing die.

Fig. 6 represents a cross sectional view of a finished case.

Fig. 7 is a fragmentary view of a punch and die.

Fig. 8 is a perspective view of one form of apparatus which may be used.

Fig. 9 is a sectional elevation of another form of apparatus which may be used.

Fig. 10 is a sectional elevation of another form of apparatus which may be used.

Fig. 11 is a graph showing the relation between particle size and concentration of solution.

In the manufacture of cartridge cases the first operation is usually to cut a disc or blank (Fig. 1) from a flat strip of metal and then to cut this disc to the form shown in Fig. 2. This is done in a single press using a blanking and cupping die or may be done in two presses or operations. The cup of Fig. 2 is passed through succeeding dies by means of a punch 20, such as shown in Fig. 7, until the proper dimensions are secured. The die is indicated at 22, die holder at 23, and the piece to be drawn is at 24. It is to be noted that there is considerable reduction of the wall thickness in each operation, which requires a large amount of work to be performed upon the case in the drawing operations. The case can be finished after the drawing is completed by placing the desired extraction groove 21 and other conventional features thereon, such as shown in Fig. 6. The example shown is a centerfire case similar to the caliber .45 cartridge with the thicknesses slightly exaggerated. If a rimfire case is to be produced, the base is folded over in a conventional manner to produce the rim in which the priming mixture is placed.

In the present invention, the case or strip before drawing, is subjected to hydrogen sulphide. This will form a coating thereon which for some unknown reason allows the drawing of steel components without undue wear on the drawing die and with excellent surfaces on the drawn components. The surface can be subjected to hydrogen sulphide by placing the article in water and bubbling hydrogen sulphide through the water, such as shown in Fig. 8, or the article can be moistened and then subjected to the hydrogen sulphide gas. In either case, an amorphous or colloidal particle size coating is formed on the article. This coating is dark and is not firmly bonded to the surface.

As the water on the surface is subjected to hydrogen sulphide gas, the gas will be absorbed thereby. The solubility of hydrogen sulphide gas in water is low, the saturated solution at 25° C. being .2 normal and the higher the temperature the less the solubility. It can be theorized that the following primary ionization takes place:

$$H_2S \rightarrow H^+ + HS^-$$

A secondary ionization then takes place as shown by:

$$HS^- \rightarrow H^+ + S^{--}$$

The value of the ionization content of the sulphide ion in a saturated solution at 25° C. is given as 1.2×10^{-15} as compared to 0.9×10^{-4} moles per liter for the hydrogen ion concentration. It is thus apparent that the conditions are such that the particle size of the ferrous sulphide as the result of the reaction of the iron ion and the sulphide ion will be in the colloidal range. This is indicated by the graph shown in Fig. 11 giving the relation between particle size and concentration, said graph being based on Von Weimarn's law.

Also the iron solubility will be low because of the low hydrogen ion concentration.

The precipitate of ferrous sulphide is hydrous which may be one of the reasons for its efficiency as a lubricant. The coating appears to be better if the water is changed frequently or possibly kept aerated.

Following this treatment, it is desirable to subject the surface to a lubricant or other material which will prevent oxidation thereof. It was found that if the surface was left exposed to the air for as little as five minutes, that rusting might occur which would interfere with the subsequent drawing operations. The time after sulfidation in which it is desirable to treat the surface to prevent oxidation, of course, will depend upon the conditions and may be longer or shorter than five minutes. The treatment to prevent oxidation of the coating formed by sulfidation may or may not have a lubricant combined therewith.

It was also found that if the article had the surface thereof pitted before sulfidation, that excellent drawing properties would result. The pitting may be obtained by treating the case with a solution containing ferric ions in sufficient quantities to attack the surface properly. One solution is that composed principally of water and ferric sulphate. One theory for the chemical action which takes place is that there is a reduction of the ferric ion to the ferrous ion by the loss of one charge. At the same time there is an oxidation reaction of the metallic iron to the ferrous ion. This may be represented by the following formula:

$$2Fe^{+++} + Fe^{\circ} \rightarrow 3\ Fe^{++}$$

There is thus a dissolution of the metal on the surface of the case. When ferric sulphate is used, the exterior surface is pitted uniformly. In the lubricating or oxidation preventing treatment any of the well known drawing lubricants may be used. One of these may be composed substantially as follows:

	Per cent
Soap	11.8
Mineral matter	0.4
Free fatty acid (as oleic acid)	9.8
Water	58.0
Mineral oil (or other oils)	20.0

As an example of one sequence of operations of sulfidating steel strips in ammunition component manufacture, the following may be used:

1. Degrease by the use of some suitable degreasing agent such as an alkali or a solvent, examples of which are caustic soda, a sodium phosphate, trichloroethylene, and other well known degreasing agents. It has been found that an alkali containing rosin gives good results. Such an agent, for example, may be composed as follows:

	Per cent
Rosin	4.75
Na_3PO_4	2.8
Na_4SiO_4	25.2
NaOH	50.0
Water	17.25

In this case the alkali solution may be heated to 180° F. and the strips placed therein for about three minutes.

2. The strips are then rinsed in hot water.

3. The surface is subjected to a ferric sulphate solution which may be made by using 5% to 15% (10% being preferable) of "Ferrisul" in water maintained at 150–180°, 160° being preferable. The strips are placed in the "Ferrisul" solution for a period of time of five to fifteen minutes although six minutes appears to be the preferable amount. "Ferrisul" is a commercially avaliable product containing about 90% ferric sulphate.

4. The strips are scrubbed and rinsed to remove all traces of the ferric sulphate solution.

5. The strips are sulfidated in any of the manners set forth hereafter.

6. The articles are rinsed.

7. The articles are lubricated with a substance such as that described previously. The articles may also have lard oil placed thereon or lard oil may be used without any other lubricant. The articles are then drawn as described previously.

Several forms of apparatus may be used for sulfidating the strip. One form is shown in Fig. 9 wherein the tank **25** contains water **26** and has a shaft **27** with a suitable handle **28** located at the exterior of the tank. The shaft **27** has a bracket **29** with clamps **30** thereon for clamping the steel strips **31** in place. The inverted container **32** has hydrogen sulphide gas introduced therein in any suitable manner. The handle **28** is turned to bring the steel strip **31** into the position shown in dotted lines at **33**. The strip is thus passed through the water and becomes moistened before it is subjected to the hydrogen sulphide gas. At temperatures of about room, a coating is produced in as little as 15 seconds but it is to be understood that the time will vary in accordance with many factors, such as cleanliness of the strip, purity of the gas, etc.

Another form of apparatus is shown in Fig. 10 wherein there is a tank **34** containing water **35**. The container **36** is supported or allowed to float on the water and hydrogen sulphide gas is introduced into the interior thereof. An endless conveyor belt **37** having means to engage the articles is used to carry the articles through the water and to the hydrogen sulphide gas in the container **36**. The articles may be removed from the belt at **38** in any suitable manner.

An apparatus is shown in Fig. 8 which may be used to immerse the steel strips in water through which hydrogen sulphide gas is bubbled. A source of hydrogen sulphide gas is indicated at **39**. A valve arrangement **40** controls the flow of gas through pipe **41** and into the distributing tube **42** at the bottom of tank **43**, tank **43** having water therein. The strips are placed in the water through the opening **44** in the hood over the top of the tank **43** and tank **45**. A blower is attached to pipe **47** for the purpose of removing the gas through passage **46** as it comes from the surface of the water in tank **43**. The pipe **47** and blower attached thereto may be arranged to pass said gas through a purifier before exhausting to a suitable place.

Any gas which is not removed by **46** and **47** will be exhausted through the upper hood **48** and by a suitable blower attached to pipe **49**. The tank **45** serves as a rinsing tank and the steel strips may be removed from tank **43** upon completion of sulfidation and immediately be transferred to tank **45** for rinsing purposes. It is apparent that other forms of apparatus may be used and that those shown are merely exemplary.

By the present invention, steel articles, such as ammunition components may be subjected

to deep drawing operations with long die life and excellent drawn surfaces.

What is claimed is:

1. In the drawing of a ferrous metal article, the method comprising the steps of producing an amorphous coating on said article by subjecting said article to hydrogen sulphide, and then shaping said article by drawing.

2. In the shaping of a ferrous metal article, the method comprising the steps of producing a coating on said article by subjecting said article to hydrogen sulphide in the presence of water, and then shaping said article by drawing.

3. In the shaping of a ferrous metal article, the method comprising the steps of producing a coating of colloidal particle size on said article by subjecting said article to hydrogen sulphide, and then shaping said article by drawing.

4. In the shaping of a ferrous metal article, the method comprising the steps of producing a drawing aid coating on said article by subjecting said article to hydrogen sulphide in the presence of water, treating said coating to substantially prevent oxidation, and then shaping said article by drawing.

5. In the shaping of a ferrous metal article, the method comprising the steps of producing a drawing aid coating on said article by subjecting said article to hydrogen sulphide in the presence of water, placing a lubricant on said coated article, and then shaping said article by drawing.

6. In the shaping of a ferrous metal article, the method comprising the steps of placing a coating of colloidal particle size thereon by subjecting said article to hydrogen sulphide in the presence of water, placing a lubricating compound on said article immediately after subjecting to the hydrogen sulphide, and then shaping said article by drawing.

7. In the drawing of a ferrous metal article, the method comprising the steps of subjecting the surface of said article to water, subjecting said moistened article to hydrogen sulphide, and then shaping said article by drawing.

8. In the drawing of a ferrous metal article, the method comprising the steps of subjecting the surface of said article to water, forming a drawing aid coating thereon having a colloidal particle size by exposure to hydrogen sulphide, applying a lubricant to said coated article, and then shaping said article by drawing.

9. In the drawing of a ferrous metal article, the method comprising the steps of forming a colloidal drawing aid coating thereon by placing the article in a bath through which hydrogen sulphide is bubbled, and then shaping said article by drawing.

10. In the shaping of a ferrous metal article, the method comprising the steps of placing thereon a drawing aid which is the reaction product of hydrogen sulphide and the iron of said article, and then subsequently shaping said article.

11. In the shaping of a ferrous metal article, the method comprising the steps of pitting the surface of said article, placing a drawing aid thereon which is the reaction product of hydrogen sulphide and the iron of said article, and then subsequently shaping said article by drawing.

12. In the shaping of a ferrous metal article, the method comprising the steps of pitting the surface of said article, placing a drawing aid thereon which is the reaction product of hydrogen sulphide and the iron of said article in the presence of water, and then subsequently shaping said article by drawing.

13. In the shaping of a ferrous metal article, the method comprising the steps of pitting the surface of said article, subjecting the surface of said article to hydrogen sulphide in the presence of water, lubricating said surface immediately thereafter, and then shaping said article by drawing.

14. In the drawing of a ferrous metal article, the method comprising the steps of subjecting the surface to be drawn to a solution containing ferric ions, placing a drawing aid thereon which is the reaction product of hydrogen sulphide and the iron of said article, and subsequently shaping said article by drawing.

15. In the drawing of a ferrous metal article, the method comprising the steps of subjecting the surface to be drawn to a ferric sulphate solution to substantially remove said surface and produce a uniform pitting thereon, subjecting said article to hydrogen sulphide in the presence of water, and subsequently shaping said article by drawing.

16. In the drawing of a ferrous metal article, the method comprising the steps of subjecting the surface to be drawn to a ferric sulphate solution, placing a drawing aid thereon which is the reaction product of hydrogen sulphide and the iron of said article, treating said coating to substantially prevent oxidation thereof, and then shaping said article by drawing.

17. In the drawing of steel ammunition components, the method comprising the steps of placing a hydrated ferrous sulphide coating on said components, and subsequently shaping said components by drawing.

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