

Oct. 31, 1950

J. WULFF

2,528,406

METHOD OF MAKING PYROPHORIC ELEMENTS

Filed June 22, 1946

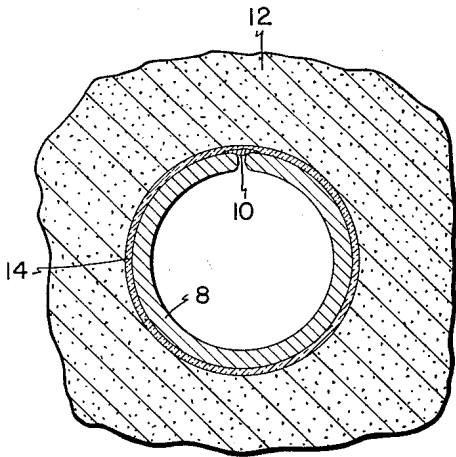


FIG. 1

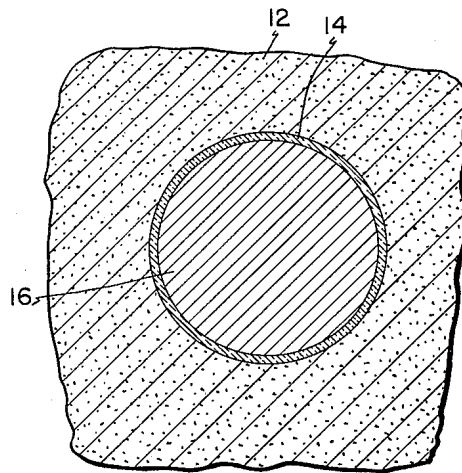


FIG. 2

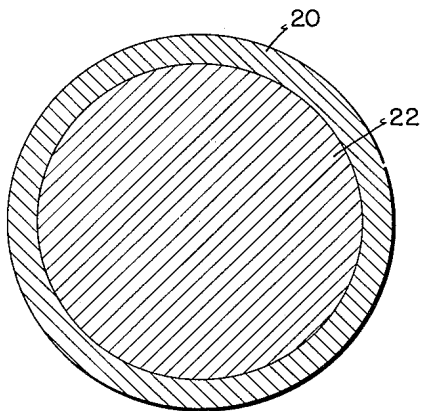


FIG. 3

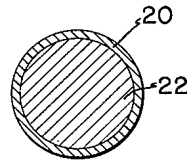


FIG. 4

INVENTOR.  
JOHN WULFF  
BY *Jenney & Hildebreth*  
ATTORNEYS

# UNITED STATES PATENT OFFICE

2,528,406

## METHOD OF MAKING PYROPHORIC ELEMENTS

John Wulff, Cambridge, Mass.

Application June 22, 1946, Serial No. 678,536

4 Claims. (Cl. 148—2)

1

The present invention relates to pyrophoric elements and methods of making the same, and is especially but by no means exclusively concerned with the manufacture of ignition or sparking devices of small diameter, often called "sparking flints," for use in cigarette lighters, torch and lamp lighters, and the like.

Sparking flints are generally made from an alloy containing one or more of the rare earth metals cerium, lanthanum, neodymium, etc. It is customary to employ misch metal, which is a mixture of the several rare earth metals, with cerium predominating. To obtain the desired sparking properties, iron is generally added to form an alloy with the rare earth metal or metals.

Methods heretofore employed for casting this pyrophoric alloy into sparking devices and small diameter flints are recognized as being unsatisfactory and expensive. According to conventional practice, the molten alloy, melted in special crucibles under a barium chloride protective cover, is poured into sheet iron tubes of approximately the same inside diameter as the desired finished size of flint. For cigarette lighter flints, the tubes may be as small as  $\frac{3}{32}$ " inside diameter. Following the casting, the iron tubes are stripped from the cast alloy and the latter then cut up into flints. The stripping process is difficult and time-consuming, and is wasteful of alloy, since the tubes tend to adhere to the alloy, and the thin rods are fragile.

One of the objects of the present invention is, therefore, to provide a new and improved method of making sparking flints and similar ignition devices, which method makes possible the rapid and economical production of small-diameter flints possessing excellent sparking properties.

More specifically, it is an object of the invention to provide a method of making sparking flints that avoids the necessity for stripping the tube from the cast flint metal following the casting.

In accordance with these objects, the casting of the melt into metal tubes or jackets is carried out under conditions that insure a highly fluid melt which rapidly and completely fills the tubes when poured. By suitable temperature control, the metallurgical structure of the jacket or tube is then so modified that its retention as part of the finished flint causes no impairment or interference with the sparking properties.

In carrying out the invention, the tubes or jackets into which the melt of rare earth metal is poured may conveniently have an outside diameter substantially corresponding to the desired size

2

of flint. Alternatively, it may be advantageous in certain applications to employ tubes having a cross-section substantially greater than the desired final size. In the latter event, following the casting, the relatively large, filled tubes are reduced to the desired cross-section by swaging, and thereafter, by suitable heat treatment, the requisite metallurgical structure is obtained.

While the invention is well adapted to making sparking devices or flints of various diameters, it is especially suited to making the small-diameter cigarette lighter flints which have been particularly difficult to manufacture by conventional methods. Accordingly, the invention will be described in connection with the making of these small-diameter flints, it being understood that such description is illustrative rather than by way of limitation to particular dimensions and cross-sectional shapes.

In the drawings illustrating the significant steps in the carrying out of the invention, Fig. 1 is a sectional view on a considerably enlarged scale of one type of tube preparatory to receiving the fill of molten alloy; Fig. 2 is a similar view following filling and heat treatment; Fig. 3 is a sectional view on an enlarged scale of another type of metal tube into which the melt has been poured; and Fig. 4 is a similar view of the same tube after swaging.

In practicing the invention according to one technique thereof, metal tubes 8 are employed having an outside diameter substantially that of the desired size of the flint. For reasons of economy these tubes are preferably formed of thin sheet metal, generally of sheet iron although materials such as nickel, copper, aluminum or the like may be employed.

Because of their manner of construction, these tubes have a narrow longitudinal seam. To prevent the escape of molten alloy through this slit or seam during the casting operation, the tubes are prepared by painting or coating the crack with a material such as aluminum flake pigment in a resinous vehicle. The flakes of aluminum serve to bridge the slit, as indicated at 10, to close the seam and provide a continuous surface for the reception of the protective coating.

The tubes are then coated externally by spraying, dipping or painting with a refractory material which combines with the investment to form a material that is relatively inert with respect to molten pyrophoric metal. An example of a suitable material is a glass such as lime glass prepared in finely divided form by ball milling to a particle size predominately below ten microns

3

and applied as a suspension to the tubes, using ethyl silicate, sodium silicate or the like as the suspending medium.

After this coating has dried, the tubes are packed in the usual iron flask and an investment, indicated at 12, poured around the tubes. A suitable investment is one predominating in alumina and previously digested with hydrochloric acid.

The flask, prior to the pouring of the melt, is heated to above 1800° F. by a suitable furnace. In this preliminary heating stage, the coating of finely divided glass is sintered with the investment to form a homogeneous coating or glaze 14 that provides an effective lining or barrier between the metal tubes and the surrounding investment.

The melt of rare earth metal, prepared according to conventional practice in a graphite crucible under a protective salt top, preferably contains some iron but less than the amount customarily provided for the usually pyrophoric alloys. As a general indication, 10% to 15% iron is ample.

The melt may advantageously be raised to a relatively high temperature for the casting, temperatures as high as 2300° F. being permissible. Upon pouring, the melt rapidly fills the passages in the jackets. By reason of the high temperature of the melt and the preheating of the mold to a temperature of above 1800° F., diffusion takes place between the metal tubes and the molten alloy within. If the initial melt temperature has been sufficiently high, or if the mold after pouring is held for some time at an elevated temperature, substantially all the metal of the tubes will become dissolved and diffused throughout the melt. As a result of such diffusion, the iron content of the alloy is raised to the desired amount for proper sparking qualities of the flints.

By reason of the coating or glaze 14 on the exterior of the metal tubes 8, a protective barrier is provided against the escape of the molten, highly active alloy, after diffusing through the tubes or jackets, into contact with the investment material surrounding the tubes. Such barrier not only prevents oxidation and contamination of the alloy, but it also results in affording a smooth exterior finish to the cast rods. The coating being continuous, it is immaterial whether the tubes employed are initially seamless, or are of seamed or rolled-up construction.

Instead of employing an initial melt temperature sufficiently high to insure that substantially all of the metal in the jackets is diffused into the melt before the temperature of the melt and mold falls below the temperature at which diffusion takes place for the then existing ratio of iron to rare earth metal, additional external heat may be provided so that the diffusion is carried substantially to completion.

The appearance of the article, in section, following the diffusion between tube 8 and fill 16 is as shown in Fig. 2. No boundary exists between the tube and the fill, since the iron or other metal of the tube has substantially diffused throughout the fill, within the barrier provided by the lining or glaze 14.

After the mold has been allowed to cool slowly, it may be broken open to separate the investment and lining from the cast rods. The lining has but slight tendency to adhere to the rods, hence the separation is accomplished with relatively little difficulty. If desired, the rods may

4

be passed through a centerless grinder or sander as a final surface-finishing operation.

As an alternative to the use of small diameter, thin wall tubes, the tubes into which the melt containing the rare earth metal is cast may be materially larger than the desired final size of the flint. Thus, for the manufacture of flints which are to have a finished cross-section of the order of 1/8" or smaller, tubes having an outside diameter of from 1/4" to 1/2" may be used. For tubes up to about 1/4", a relatively thin wall thickness, corresponding to about 16 gauge, may be employed. For the larger outside diameters, where the subsequent reduction by swaging is to be more severe, a somewhat thicker wall is desirable. In general, a suitable wall thickness is that which provides somewhat more than 30% of the total weight of the cross section after the tube has been filled with the melt. The tubes should be of seamless construction, and of iron or nickel, with iron generally being employed.

In carrying out the casting, certain precautions must be taken to prevent voids, since these give rise to cracking of the tubes in the subsequent swaging operation. Casting techniques which substantially eliminate voids are those in which escape of the air is facilitated and turbulence minimized. Vacuum and tilt casting methods are well suited to accomplish this.

Following the casting operation, the tubes 20 containing the rare earth metal fill 22 are subjected to swaging treatment, employing standard swaging techniques and apparatus. By the swaging operation, the jacketed rods are reduced in diameter to substantially the desired diameter for the finished flints. Several passes through the swaging machine are generally required to enable the reduction to be carried out in small steps. As many as eight passes may be desirable where a substantial reduction in diameter is to be accomplished, as from 1/2" down to 3/8" outside diameter. The reduction in diameter during the swaging naturally causes a marked increase in length, so that a relatively long rod results from the initially shorter but larger diameter tube and therefore more easily filled tube.

The swaging may be carried out hot, using rods heated to between 1000° F. and 1500° F., a temperature of approximately 1400° F. being suitable. On the other hand, the swaging may be done cold, with highly satisfactory final results and general simplification of the swaging operation. Because of the brittle character of the rare earth metals, the swaging, when done on unheated rods, causes a certain amount of crumbling or breaking up of the metal within the jacket. However, the nature of the swaging operation is such as to cause the jacket to maintain compressive forces on the metal within the tube, during the process of transverse contraction and axial elongation.

To impart satisfactory sparking properties to the swaged and jacketed rod, appropriate heat treatment is required. In most instances, this will be carried out in a manner that not only causes the rare metal fill to be remelted, but also results in substantial diffusion between the jacket metal and the fill, thereby enhancing the iron content of the pyrophoric alloy.

The heat treating operation is preferably carried out with the axis of the tube substantially vertical, in order that there may be no voids as the crumbled and cracked fill melts into a compact mass. Furthermore, if local heating, as by

5

induction or resistance heating, is employed for the heat treatment, the travel of the hot region should be from bottom to top of the tube. Thus, the tube may be lowered through a high-frequency heating coil which rapidly brings the temperature of the rare earth metal to the melting point, beginning at the bottom and progressing upwardly. The tube ends should be plugged or crimped to seal off the rare earth metal fill.

Since it will generally be found advantageous not only to carry out the swaging on unheated articles, but also to employ for the casting a melt that is deficient in iron in terms of good sparking quality, the heat treatment will in most cases involve not merely raising the temperature above the melting point of the fill, but also providing the proper conditions of time and temperature for appreciable diffusion between the fill and the tube or jacket. By way of example, an anneal at 1800° F. for about fifteen minutes will generally provide adequate diffusion between the jacket metal and the molten fill. It is not practical to effect complete diffusion of the jacket metal, however, since the molten fill may sweat out locally and escape through the jacket, even though the temperature be maintained below the actual melting point of the iron tube.

Alternatively, the filled and swaged tubes may be cut up into convenient lengths and coated on their outer surface with the protective glass or glazing composition above described and packed in graphite or refractory investment with the tube ends suitably plugged. Upon heating to 1800° F. or above, the coating is converted to a homogeneous barrier relatively inert to the pyrophoric alloy, thus permitting diffusion between molten alloy and the tube to be carried substantially to completion without risk of sweat-out and escape of the pyrophoric melt.

In those cases where diffusion has not been carried substantially to completion, it is preferable to remove the outer portions of the tube metal, in order that the soft, undiffused portions may not interfere with proper sparking qualities of the flints. Removal of this outer portion may readily be accomplished by a centerless grinding or a sanding operation.

I have thus described as my invention methods of making pyrophoric elements wherein the metal tubes into which the pyrophoric melt is poured are thereafter incorporated in the melt, either wholly or to a substantial degree, by alloying therewith, thus eliminating the need for stripping the tube from the fill following the casting operation.

I claim as my invention:

1. The method of making sparking flints from pyrophoric rare earth alloy which comprises coating the exterior of a metal tube with a material relatively inert to a pyrophoric melt, surrounding the exterior of the coated tube with an investment, heating the tube and investment to convert the coating to a relatively homogeneous protective barrier between tube and invest-

6

ment, casting a melt of pyrophoric rare earth alloy into the tube, and maintaining the alloy in molten condition within the tube until diffusion and alloying between the tube and the fill has proceeded substantially through the tube to the protective barrier.

2. The method of making sparking flints from pyrophoric rare earth alloy which comprises applying to a thin-wall metal tube having a seam a metallic flake composition to bridge said seam, coating the exterior of the tube with finely divided glazing material, surrounding the exterior of the coated tube with an investment, heating the tube to convert the coating to a homogeneous glaze to form a protective barrier between tube and investment, casting a melt of pyrophoric rare earth alloy into the tube, and maintaining the alloy in molten condition within the tube until diffusion and alloying between the tube and the fill has proceeded substantially through the tube to the protective barrier.

3. In the manufacture of small-diameter sparking flints from pyrophoric rare earth metal, the steps of casting molten pyrophoric metal into a tube of metal of the iron group, and thereafter applying heat to the filled tube in the presence of an inert protective coating on the exterior of the tube to effect diffusion and alloying between the pyrophoric metal and the tube, the diffusion and alloying being carried substantially to completion to the protective inert coating on the exterior of the tube.

4. In the manufacture of small-diameter sparking flints from pyrophoric rare earth metal, the steps of casting molten pyrophoric metal into a tube of metal of the iron group, swaging the filled tube to reduce the cross-section thereof, and thereafter applying heat to the filled tube in the presence of an inert protective coating on the exterior of the tube to effect diffusion and alloying between the pyrophoric metal and the tube, the diffusion and alloying being carried substantially to completion to the protective inert coating on the exterior of the tube.

JOHN WULFF.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
852,671	McArthur et al. _____	May 7, 1907
865,562	Brabrook _____	Sept. 10, 1907
997,801	Gebhard _____	July 11, 1911
1,217,581	Eldred _____	Feb. 27, 1917
1,290,010	Hirsch et al. _____	Dec. 31, 1918
1,551,590	Stresau _____	Sept. 1, 1925
2,066,247	Brownback _____	Dec. 29, 1936

#### FOREIGN PATENTS

Number	Country	Date
485,710	France _____	Nov. 8, 1917