

# UNITED STATES PATENT OFFICE

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## METHOD OF MANUFACTURING THIN WIRES

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My invention relates to a method of manufacturing thin wires, tapes, or ribbons or other filamentary material consisting of conducting material, as well as to objects made of such wires or ribbons or tapes. The process involves, in general, a pickling or reaction of the material with a gas or vapor at a low pressure, hereinafter referred to as the pickling or reacting gas.

Mechanical treatments, such as wire drawing, permit the manufacture of conducting wires (tungsten wire for instance) of a thickness of about 7 microns. The method of cathode, volatilization, in which the wire is subjected to ion bombardment, permits the manufacture of even thinner wires. However, the application of this latter method entails practical difficulties.

It is also known how to manufacture thin platinum wires by the application of Wollaston's process, in which process a platinum wire is covered with a silver sheath, after which the wire, together with its sheath, is rolled, and the sheath finally removed by a chemical agent. Wollaston's method has the disadvantage that the drawn wire is hard to manipulate, and for this reason it is preferable to employ a method which makes it possible to reduce the wire diameter after the wire is mounted in position.

The pickling or reaction method mentioned above enables the attainment of this result. It is known that a tungsten wire may be subjected for a certain time to a very active mordant or scouring agent (see German Patent 432,876). By this method it is possible to reduce the wire diameter from 50 microns and less to about 5 microns. However, it is impossible to obtain thinner wires, for during the reaction or mordanting the wires are subjected to rather considerable strains. These strains may be avoided by performing the reaction or mordanting in a gas or a vapor at low pressure. It is known to heat a tungsten wire to red heat in low-pressure phosphorous vapor by having an electric current flow through the said wire. The tungsten atoms combine with the phosphorous at the periphery of the wire, and this results in a reduction in the wire diameter (see German Patent 201,461).

The invention consists in an improvement of this last mentioned method. It has been noted that the application of the method specified hereabove does not permit reduction of the wire diameter to less than 5 microns. If the pickling or mordanting is carried further, the wire is likely to break. The invention furnishes a means of obtaining wires of a diameter of less than 5 microns, and it is based on the idea that in the

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known method of mordanting or pickling in low-pressure gas or vapor, the breaking of the wire is brought about by the following phenomenon:

Should the wire be pickled to a greater degree at one point than the other by accident, then the resistance would increase at that point, thus producing a temperature rise thereat. At the rather low temperature which has been employed heretofore, this temperature rise accelerates the pickling or mordanting, so that at that particular spot the wire will become a little thinner, which again will produce an additional temperature rise, and so on, until the wire breaks.

The invention is based on the fact that there exists a zone of high temperatures at which the above-mentioned phenomenon does not occur, since in that zone the temperature coefficient of the mordanting action is negative so that when the temperature rises, the pickling or mordanting becomes slower. Therefore, according to the invention, the pickling is performed at a temperature at which the temperature coefficient of the pickling action is zero or negative.

The existence of a negative temperature coefficient of pickling can be explained as follows: At high temperatures, the impacts of the molecules of the pickling-gas with the wire to be pickled have the nature of fully elastic collisions, so that the gas molecules can combine with the atoms of the wire only during a very short time. In practice, the temperature at which the temperature coefficient is zero lies at about 1500° C., and this is why the method according to the invention is preferably applicable to wires or ribbons consisting of a material whose melting point is very high.

To obtain a regular and even mordanting or pickling, it is desirable that the same number of molecules should reach every point of the wire to be treated during each time unit. This result may be obtained by arranging that there is only slight probability of an impact between molecules of the scouring gas and molecules leaving the wire surface, which are formed by reaction of the wire material with the scouring gas. Such impacts, in effect, hinder the arrival of the pickling-gas molecules on the wire surface. For this reason, the pressure of the pickling-gas is preferably so low that the length of the mean free path of the pickling-gas molecules is at least ten times longer than the dimensions of the body which is to be pickled or mordanted. In practice, the pressure of the pickling-gas is less than 50 baryes for that particular reason.

To prevent impacts between the molecules of the compound formed at the wire surface, and

the molecules of the pickling-gas, it is also desirable that the length of the free path of the pickling-gas molecules be large as compared to the dimensions of the vessel or container within which the pickling takes place. However, this container must not be so narrow as to give rise to capillary effects. Hence, the pressure in the container must be uniform at all points.

It must be noted that the reaction between an incandescent metal and a gas has already been mentioned in Langmuir's research papers (see, for instance, *Journal of the American Chemical Society*, 37, 1915, p. 1139).

During the pickling or mordanting, the pressure of the pickling-gas preferably should be kept constant. Should the container in which the process takes place be too small for this condition to automatically occur, it is necessary to add gas during the pickling. The additional reacting gas may be supplied from a suitable source of supply thereof such as, for example, a substance which, when heated, will liberate the reacting gas. When the reaction between the material and reacting gas is accomplished by means of oxygen for example, the substance acting as the source of supply of additional reacting gas may comprise potassium chlorate. Control of the heating of this potassium chlorate then permits of the pressure being maintained constant.

For the pickling of tungsten or molybdenum wires or ribbons, the pickling gas may be either oxygen or water vapor. When pickling tungsten wires, it is advisable to employ a pickling-gas that does not contain carbon, for the presence of the latter might considerably increase the resistivity of the tungsten. When pickling platinum wires, the pickling gas may be chlorine, while carbon wires are preferably pickled in oxygen.

It should be noted that the ends of the wire to be pickled are more subject to cooling than the center thereof. When the center portion of the wire has attained the required temperature at which the temperature coefficient of pickling is negative, the temperature of the ends may be lower by such an amount that near these ends the temperature coefficient of pickling will be positive at such points, with the result that the wire breaks near the ends. This phenomenon does not manifest itself in the pickling of metal wires, for instance tungsten or molybdenum wires, for these materials are good conductors of heat, with the result that the cooling of the ends of such wires will not be very pronounced. On the contrary, when carbon wire is pickled, breakage will generally occur near the ends thereof because carbon is a poor conductor of heat. Hence, when manufacturing thin carbon wires, it is necessary to proceed by steps. In such case, one starts with a wire whose length is greater than that required, and this wire is first pickled until breakage occurs adjacent an end thereof. Then the center portion of that wire is used and it is subjected to a second pickling. If necessary, a third pickling operation may be carried out.

In the manufacture of thin tungsten or molybdenum wires, in which manufacture the above phenomenon does not manifest itself, the obtainable diameter is controlled by the dimensions of the crystals. The applicant has noted that in the case of an excessive scouring, the wire will break at the joint between two crystals. To obtain very thin wires, one may pro-

ceed in two different ways. One may start with wire which comprises only one crystal. To this end, the wire is subjected to a preliminary treatment in which it is annealed to a temperature below the re-crystallization temperature (1800° C., for instance), and then the temperature is slowly raised to the re-crystallization temperature. As an alternative, attempts may be made to obtain a crystalline structure which is as fine as possible. In this case, the junctions are always over-lapped by other crystals. To this end, a preliminary treatment must be employed wherein the wire of very fine crystalline structure is rapidly heated to the re-crystallization temperature of about 2500° C.

The method according to the invention offers the considerable advantage of enabling the pickling to be performed while the wire or ribbon is duly positioned or mounted in place. Thus, in the manufacture of incandescent lamps and similar objects, the pickling may be even performed in the bulb or tube which contains the wire.

It is preferable to heat the wire to the required temperature by means of an electric current. In this case it is advantageous to keep the voltage constant, which can be obtained, for example, by means of a very high auxiliary resistance. The strength or density of the current flowing through the wire then provides a measure of the diameter obtained. It is also possible to heat the wire by means of a high frequency electric field.

The method according to the invention is very rapid. A few minutes, in general, will suffice for the wire to attain the required diameter. However, the lower the pressure of the pickling gas, the longer will be the period of time required for the completion of the process.

The process according to the invention enables the manufacture not only of wires or ribbons, but also objects consisting of wire or ribbon, for instance the grids of electron tubes. To manufacture these grids, comparatively thick wires are first wound and these wires are then subjected to a pickling process in accordance with the invention. Also, there is a form of incandescent lamp in which the filament consists of a conductor which is obtained by the weaving or braiding of a certain number of thin wires. These filaments may be produced by starting with comparatively thick wires which are then pickled, according to the method of the invention until the wires have attained the required small diameter. The above mentioned grids and filaments can be pickled within the lamp bulb or container.

Wires or ribbons manufactured according to the method of the invention may be used as filaments in small incandescent lamps, or also as suspension wires in torsion meters. Thermocouples constitute a particularly interesting field of application of the invention. To this end, the platinum wire, obtained according to Wollaston's method, may be welded or brazed to a relatively thick tungsten wire, after which the tungsten wire may be heated in the thermocouple bulb, which contains oxygen, until the required small diameter is obtained. The two filaments of the thermocouple may be manufactured by use of the method according to the invention.

The practical application of the invention has proved that heating a wire of 10 micron diameter in an oxygen atmosphere at a pressure of 10 baryes permits the reduction of the diam-

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eter to 3 microns, and even down to 1.3 microns, for example. After the pickling, the wire shows no traces of any initial variations in the wire diameter.

In the appended claims, the term "filamentary material" is intended to include wire, ribbons, tapes and any other like material of more or less regular cross-section throughout its length.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of reducing to minute size electrically conductive filamentary material of a single element of relatively high fusion temperature which comprises, heating the material by the passage of an electric current there-  
through in a surrounding atmosphere of a gas which is reactive with respect to the said material, at a low pressure of less than approximately 50 baryes, while maintaining the pressure of said gas approximately constant and maintaining the heated material at a temperature which is below its fusion point and at which the temperature coefficient of the reaction of said material with the gas is zero or negative until the desired minute size is attained.

2. The method according to claim 1 wherein the reacting gas is at a pressure of less than approximately 50 baryes and the filamentary material is maintained at a temperature of about 1500° C. during the reaction thereof with said gas.

3. The method of reducing to minute size filamentary material of a single element of the group consisting of tungsten and molybdenum which comprises, heating the said material by the passage of an electric current therethrough in a surrounding low-pressure atmosphere of a gas which is reactive with respect to the said material of the group consisting of oxygen and water vapor at a pressure less than approximately 50 baryes while maintaining the pressure of said gas approximately constant and maintaining the heated material at a temperature which is below its fusion point and at which the temperature coefficient of the reaction of said material with the said gas is zero or negative until the desired minute size is attained.

4. The method of reducing platinum filamentary material to minute size which comprises, heating the said material by the passage of an electric current therethrough in a surrounding atmosphere of chlorine gas at a low pressure less than approximately 50 baryes while maintaining the pressure of said gas approximately constant and maintaining the heated material at a temperature which is below its fusion point and at which the temperature coefficient of the reaction of said material with the said gas is zero or negative until the desired minute size is attained.

5. The method of reducing carbon filamentary material to minute size which comprises, heating the said material by the passage of an electric current therethrough in a surrounding atmosphere of oxygen gas at a low pressure less than approximately 50 baryes while maintaining the pressure of said gas approximately constant and maintaining the heated material at a tem-

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perature which is below its fusion point and at which the temperature coefficient of the reaction of said material with the said gas is zero or negative until the desired minute size is attained.

6. The method of producing electrically conductive filamentary material of relatively high fusion temperature and of minute size which comprises, forming a filamentary material constituted by a single crystal only, annealing the said material at a temperature below its recrystallization temperature and then raising the temperature slowly to the said recrystallization temperature, and heating the said material by the passage of an electrical current therethrough in a surrounding atmosphere of a gas which is reactive with respect to the said material, at a low pressure of less than approximately 50 baryes, while maintaining the pressure of said gas approximately constant and maintaining the heated material at a temperature which is below its fusion point and at which the temperature coefficient of the reaction of said material with the said gas is zero or negative until the desired minute size is attained.

7. The method of producing electrically conductive filamentary material of relatively high fusion temperature and of minute size which comprises, forming a filamentary material of very fine crystalline structure, heating the said material rapidly to its recrystallization temperature, and heating the said material by the passage of an electric current therethrough in a surrounding atmosphere of a gas which is reactive with respect to the said material, at a low pressure of less than approximately 50 baryes, while maintaining the pressure of said gas approximately constant and maintaining the heated material at a temperature which is below its fusion point and at which the temperature coefficient of the reaction of said material with the gas is zero or negative until the desired minute size is attained.

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