Jan. 4, 1955 R. A. STAUFFER 2,698,810

COATING PROCESS

Filed Aug. 25, 1950

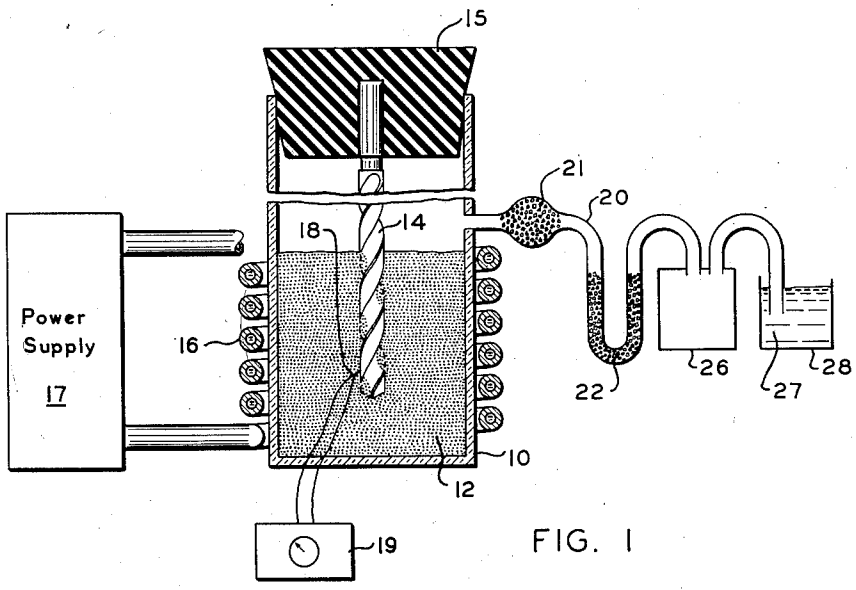


FIG. 1

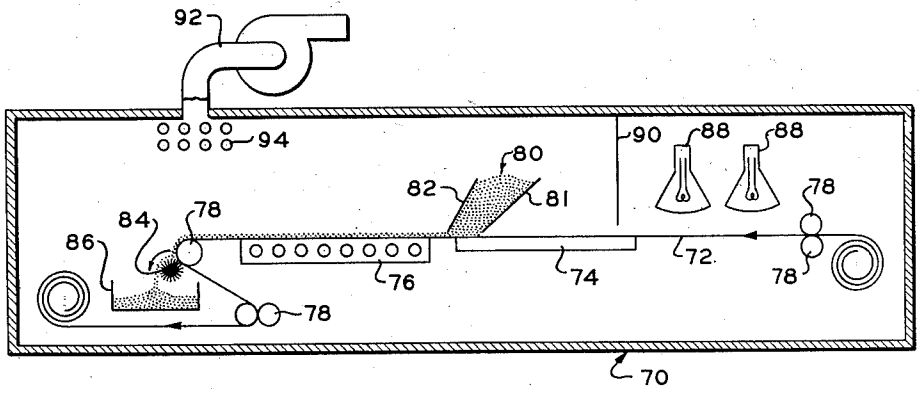


FIG. 2

INVENTOR.
Robert A. Stauffer

BY *Oliver W. Hayes*

ATTORNEY

United States Patent Office 2,698,810 Patented Jan. 4, 1955

2,698,810

COATING PROCESS

Robert A. Stauffer, Weston, Mass., assignor to National Research Corporation, Middlesex County, Mass., a corporation of Massachusetts

Application August 25, 1950, Serial No. 181,373

3 Claims. (Cl. 117—22)

This invention relates to coating and more particularly to the coating of uniform thin layers comprising group VI*a* metals. This invention has particular utility in connection with the production of coatings of chromium, tungsten, and molybdenum, which are useful as decorative coatings, corrosion-resistant coatings, or as conductive films, and which are particularly useful for increasing the cutting speed and wear resistance of cutting tools.

A principal object of the present invention is to provide new and improved processes for coating individual articles or flexible substrates with thin uniform films comprising tungsten, molybdenum or chromium.

Still another object of the invention is to provide such coating processes which are cheap, simple, and extremely rapid.

Still another object of the invention is to provide such coating processes which require a minimum of capital equipment and which can be operated by unskilled personnel.

Still another object of the present invention is to provide a process for tremendously increasing the cutting speed and wear resistance of a cutting tool by a process which adds only a very minor additional cost to the cost of the cutting tool.

Still another object of the present invention is to provide improved processes for increasing the wear resistance of machine parts, such as bearings, dies and the like.

Still another object of the present invention is to provide an improved coating powder for use in the above processes.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the products possessing the features, properties and the relation of components, and the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic, schematic, sectional view of one preferred form of apparatus for practicing the present invention; and

Fig. 2 is a diagrammatic, schematic view of another embodiment of the invention.

The invention generally relates to the formation, on various articles, of thin uniform films comprising group VI*a* metals. In the copending application of Clough and Godley filed on even date herewith there is described a process for coating articles by decomposition of the solid group VI*a* metal carbonyls on the surface of the article to be coated. The present invention is an improvement over the processes described in the above Clough and Godley application.

In the present invention the coating step is also achieved by the use of a carbonyl of a group VI*a* metal, this carbonyl being preferably in the form of a powder. However, this powder is intermixed with a filler which has a melting point considerably higher than the melting point of the carbonyl. This filler is preferably inert to the carbonyl so that there is no reaction between the carbonyl liquid or carbonyl vapors generated during the coating operation. The mixture of the carbonyl powder

and the powdered filler is preferably held in close contact with the surface of the article to be coated, and at least the surface of this article is heated to a temperature above the decomposition temperature of the carbonyl.

In one preferred embodiment of the invention the mixture of carbonyl and filler is placed in a suitable container, and the article to be coated, for example a drill, is inserted into the powdered mixture so that all surfaces of the drill to be coated are in intimate contact with the powdered mixture. The drill is then heated, for example by induction heating, so that at least the surface thereof attains a temperature of above 130° C., preferably in the neighborhood of 150° C. This temperature is maintained for about 5–15 seconds at which time the drill is removed from the powder. When the drill is heated, as above, the heat is transferred from the drill to the powdered mixture serving to melt and vaporize some of the carbonyl in contact therewith, this carbonyl diffusing to the surface of the drill where it is decomposed to form a thin uniform layer comprising the group VI*a* metal.

The primary function of the filler material is to prevent undue agglomeration of the carbonyl powder when subjected to the heat from the drill. This permits the use of one batch of the powder for coating a number of articles, thereby achieving a considerable saving of the relatively expensive carbonyl. The filler seems to have the additional advantage of preventing an unduly rapid escape of carbonyl vapors from the vicinity of the generation thereof (i. e., the interface between the drill and the powdered mixture).

Referring now to Fig. 1 there is shown one schematic, diagrammatic representation of one preferred embodiment of the invention, as applied to the coating of a drill, for example. In this figure, **10** represents a container which confines a quantity of the powdered mixture **12**, this container being closed by a stopper **15**. The drill, schematically indicated at **14**, is heated by a high-frequency induction coil **16** connected to a suitable power supply **17**. If desired, a thermocouple **18** may be utilized for indicating, by means of a meter **19**, the temperature of the drill during the treatment thereof. The container **10** is preferably vented through a tube **20**, containing a quantity of copper oxide **21**. The tube **20** also includes a calcium chloride vapor barrier **22**, a pressure surge tank **26**, and another container **28**, the end of the tube **20** being below the level of a water solution of potassium hydroxide **27** held in container **28**.

In one preferred example of the process of the present invention, the powdered mixture **12** is prepared by powdering chromium carbonyl, $Cr(CO)_6$, to which is added an approximately equal quantity, by weight, of alumina as a filler. The crushed grains of carbonyl powder are preferably of a size at least as small as 60 mesh, this small grain size being particularly desirable for small drills, taps and the like where there are small grooves to be coated. The powdered mixture **12** is then placed in the container **10**. A drill **14** to be coated is cleaned, such as by washing in acetone or by vapor degreasing, and is inserted in the powdered mixture, the drill being twisted as it is inserted so as to force the powdered mixture into the flutes of the drill. The container **10** is preferably tapped to insure uniform contact between the powder and the drill. The high-frequency coil **16** is then energized to heat the drill to a temperature of approximately 150° C., this temperature being preferably maintained for about 5 seconds. One convenient method of operating the apparatus of Fig. 1, without the use of thermocouples for directly reading the drill temperature, is to replace the potassium hydroxide solution **27** with water and then to energize coil **16** until bubbles appear in the water **27**. This indicates that decomposition of the carbonyl is taking place, the bubbles being carbon dioxide. The coil is deenergized and the drill is allowed to cool slightly for a few seconds. The coil is energized again until another group of bubbles appears in water **27**. Again the power is turned off. This cycle can be repeated for 3–6 times to give a very satisfactory coating. At the end of this above coating period the coil **16** is deenergized and the drill is removed. The drill is now ready for use, no additional treatment being necessary other than the removal

of those few particles of alumina and carbonyl which may adhere thereto.

Tests made on high speed drills, which have been given a chromium coating by the above techniques, have shown a very substantial increase in both cutting speed and wear resistance. A number of uncoated drills were tested by drilling ¼ inch holes through a ¾ inch block of #347 stainless steel, no lubricant being used to expedite the test. These drills were under a constant load and were run with a constant speed. The average number of holes drilled by the uncoated drills was 9. An equal number of similar drills were coated as above and subjected to the same test. The average number of holes drilled by the coated drills was 15. In addition to their greater life the coated drills had on the average a much higher cutting speed than did the uncoated drills. For example, the average cutting speed of the coated drills after having drilled three holes was 68 seconds, while the average cutting speed for the uncoated drills after having drilled three holes was 84 seconds.

It should be pointed out that the apparatus of Fig. 1 is particularly desirable where the coating operation is carried out in an unventilated room, since any carbonyl vapors which might be generated during the coating process are trapped and condensed either in container **10** or tube **20**. Additionally, carbon monoxide generated during the decomposition is converted to carbon dioxide by being passed over the copper oxide **21** which is heated to 320° C. This carbon dioxide is absorbed in the potassium hydroxide solution. When an open container **10** is used it should be employed under a ventilating hood since carbonyl vapors are considered to be quite toxic.

While a preferred embodiment of the invention has been discussed above, numerous modifications thereof may be made without departing from the scope of the present invention. For example, the percentage of the filler employed in the powdered mixture may range from about 10% of the mixture to about 70% of the mixture. With the low percentage of filler there is a tendency to obtain agglomeration of the powder during use thereof. However, even the smaller percentage of filler assists in breaking up these agglomerations to permit reusage of the powder. The higher percentage of filler tends to given more uneven coatings, but these disadvantages may be overcome by jiggling the article, during coating or between coating stages, so as to agitate the powder in the neighborhood of the article to bring fresh powder into contact therewith.

Equally, the carbonyls of tungsten and molybdenum may be used in place of the carbonyl of chromium. These carbonyls do not appear to give quite as good results with respect to increasing cutting speed and wear resistance of the cutting tool. However, the resultant tungsten or molybdenum films are more advantageous for certain uses. For example, these coatings are particularly advantageous for high-temperature resistant materials and corrosion-resistant materials. In using molybdenum carbonyl the temperature of the surface of the article to be coated should be on the order of about 160° C., while for tungsten carbonyl the temperature is preferably on the order of about 170° C. These temperatures are not critical but it is preferred to operate at temperatures not much in excess of 180° C. At temperatures above 180° C. the carbonyl powder adjacent the article surface is vaporized very rapidly and the coating reaction seems to be greatly accelerated. This gives a much thicker coating and tends to waste the relatively expensive carbonyl. This fast coating is, additionally, more difficult to control accurately. It has been found, particularly in the manufacture of coatings for abrasion-resistant purposes, that the thicker coatings achieved at the higher temperatures appear to give poorer results. However, corrosion-resistant coatings obtained at these higher temperatures, with their resultant thicker coatings, are often more advantageous.

In the preferred processes described above, the article to be coated has been shown as being heated while in contact with the powdered carbonyl mixture. While this is a preferred system operation, it is not essential to the process. For example, the article to be coated may be heated slightly above the desired operating temperature prior to insertion into the powdered mixture and can then be inserted in the mixture before any substantial cooling takes place. This method of operation is particularly suitable where the article to be coated has a relatively large volume of considerable heat storage capacity so that the temperature drop during the coating process is not unduly great.

While the invention has been described particularly with respect to its utility in connection with coating steel tools, it has innumerable other uses. For example, all types of cutting tools may be advantageously coated and coatings may be applied by the processes, as described above, on other materials such as machine parts, glass, plastics and the like. Equally, other metals may have coatings applied thereto to increase their corrosion resistance, to alter the electrical characteristics of their surfaces, and for numerous other purposes.

In many cases it is highly desirable to coat continuous substrates with metals, and the present invention is particularly adaptable for accomplishing such coatings. Such coatings can be applied by techniques, to be described hereinafter, to a large group of materials such as metal sheets, plastic substrates, fabrics and the like. In Fig. 2 there is shown one embodiment of the invention which employs the above described techniques for applying metallic coats to long strips of flexible substrate. In this embodiment of the invention the substrate is moved past a station for applying the mixture of the inert filler and the metal organic powder to the substrate, this powder being applied in the form of a thin uniform film of the solid, finely divided, powdered mixture. The powder-carrying substrate is thereafter moved past a heating station where at least the surface of the substrate is heated to a temperature above the decomposition of the metal organic powder.

In the Fig. 2 embodiment of the invention the metal organic powder preferably comprises a mixture of an inert filler and a powdered metal carbonyl, preferably a powdered carbonyl of a group VI*a* metal. In the apparatus illustrated in Fig. 2 there is provided a coating chamber **70** in which there is positioned a roll of the substrate **72** to be coated. A pair of platens **74** and **76** support the substrate during its passage through the coating chamber, platen **76** being arranged so that it can be heated to a temperature above the decomposition temperature of the carbonyl. Suitable advancing and guide rolls **78** are provided in various locations within the coating chamber for assisting in moving the substrate **72** through the coating chamber **70**. A supply of the carbonyl powder mixture **80** is shown as being held in a hopper **81** so that the powdered mixture may be spread by means of a doctor blade **82** in a thin layer onto the surface of the substrate **72** as this substrate moves past the doctor blade **82**. A brush **84** is provided for removing the powdered mixture remaining on the substrate **72** after the coating operation, this excess powdered mixture falling into a bin **86** which may, if desired, be returned to hopper **81**. If desired, an additional heating means, illustrated as heat lamps **88**, may be provided for preheating that surface of the substrate **72** which is to be coated by decomposition of the carbonyl. In a preferred form of the invention there is provided a vapor shield **90** between the heat lamps **88** and the remainder of the interior of the coating chamber. The coating chamber **70** preferably also includes an exhaust system **92** in front of which there is positioned a cooling coil **94** which is arranged to condense any carbonyl vapors which might otherwise be withdrawn by the exhaust system **92**.

In the use of the Fig. 2 embodiment of the invention substrate **72** is positioned in the coating chamber and a supply of the carbonyl powder mixture is placed in the hopper **81**. Platen **76** is then heated, for example by steam, to a temperature on the order of 150° C. If desired, heat lamps **88** may also be energized to preheat the substrate as it moves through the apparatus. In a preferred embodiment of the invention the preheating of the substrate is limited to a temperature less than about 120° C. As soon as the above heating means are placed in operation the substrate is advanced through the coating device by means of rolls **78**. During this advancement the doctor blade applies a layer of powdered mixture **80** to the surface of the substrate, this powder layer being approximately 1/16 inch thick and being substantially uniformly spread over the surface of the substrate to be coated. As the powder-coated substrate passes across the highly heated platen **76**, the substrate becomes heated to about 150° C. thereby decomposing

at least that portion of the powdered carbonyl which is in intimate contact with the surface of the substrate, thus forming the metal coat thereon. As the coated substrate passes the brush 84 the remaining powdered mixture is brushed off. Any undecomposed carbonyl vapors generated by heating of the carbonyl above its decomposition temperature are trapped by cooling coils 94 so that they may be recovered for subsequent use. By means of the above apparatus and method numerous substrates may be coated with various metals by the decomposition of metal organics, and particularly by the decomposition of the group VI*a* metal carbonyls.

While alumina has been described as a particularly suitable filler material, numerous other fillers may be employed, such as the refractory oxides, refractory silicates, and other materials which are relatively inert at the decomposition temperatures employed.

In some cases it may be desirable to deposit two of the group VI*a* metals at one time, these two metals creating a codeposition or alloy as they are formed on the surface of the article being coated. To accomplish this result it is relatively simple to modify the powered mixture referred to above by adding two carbonyls instead of a single carbonyl.

The coatings obtained by the present invention appear to comprise substantially pure group VI*a* metals, although it is possible that some oxide or carbide may be present. These coatings are extremely tough and adherent and cannot be stripped from the article by mechanical force. The thickness of the coatings produced in accordance with the processes described above appears to be on the order of less than one micron (.00004 inch). The exact mechanism of the coating reaction is not completely understood and it appears to be a combination of gas phase, liquid phase, and solid phase reactions between the carbonyl immediately surrounding the article and the surface of the article. There is some evidence to indicate that, when coating ferrous articles, the coating reaction is at least partially a replacement reaction, the iron at the surface of the article being replaced by the group VI*a* metal resulting from the carbonyl decomposition. This effect has been particularly observed with chromium coatings wherein a drill coated in accordance with the procedure of Fig. 1 has been found to have lost weight during the coating.

In some cases it is desired to coat various articles with compounds of the group VI*a* metals rather than with essentially pure group VI*a* metals. In such cases this compound coating may be readily achieved by providing, in addition to the carbonyl, another material which may be readily decomposed by heat to make available an atom for combining with the group VI*a* metal being coated. One example of such a process is the formation of moylbdenum disilicide coatings upon various articles, for example turbine blades for high temperature operation. In this modification of the invention the turbine blade is inserted into a powdered mixture of inert filler, such as alumina, and molybdenum carbonyl. This mixture is then evacuated to a low free air pressure and is saturated with a silane vapor. The turbine blade is then heated, preferably by induction, to a temperature on the order of 160° C. to decompose the molybdenum carbonyl and the silane vapor in contact therewith. Silicon and molybednum are deposited on the heated surface of the turbine blade under these conditions, the turbine blade being subsequently heated in vacuum to form an extremely high-temperature resistant molybdenum disilicide coating on the surface of the turbine blade as described in the above mentioned copending application of Clough and Godley.

The expression "group VI*a* metals" is intended to include those metals in group VI*a* shown on the "Periodic Chart of the Atoms" W. F. Meggers, 1947 Edition, published by W. M. Welch Manufacturing Company.

Since certain changes may be made in the above products and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of coating the surface of a material with an adherent layer comprising a group VI*a* metal, said process comprising the steps of contacting said surface of said material with a mixture of a powdered inert filler material and a powdered solid carbonyl of said metal, said inert filler material being a heat insulator and having a melting point considerably higher than the decoposition temperature of the carbonyl and being inert to said carbonyl at said decomposition temperature, said mixture comprising approximately 10% to 70% by weight of said filler material, and maintaining said surface at a temperature at least as high as the decomposition temperature of said carbonyl for a sufficient length of time to form said layer, said temperature being sufficiently low so that the carbonyl is maintained between about 130° and 180° C. so as to be below its melting point and solid carbonyl remains adjacent the surface, the total pressure over said carbonyl being maintained at about atmospheric pressure during decomposition of said carbonyl.

2. The process of claim 1 wherein said material to be coated comprises a flexible substrate and a layer of the mixture of powdered carbonyl and inert filler is spread across the surface of the substrate.

3. The process of claim 1 wherein said inert filler is electrically insulating, said material is a conductor of electricity and said material is heated by induced electrical currents.

References Cited in the file of this patent

UNITED STATES PATENTS

1,365,499	Kelley	Jan. 11, 1921
1,497,417	Weber	June 10, 1924
2,046,629	Ihrig	June 25, 1934
2,041,480	Oexmann	May 19, 1936
2,099,874	Trenzen	Nov. 23, 1937
2,523,461	Young	Sept. 26, 1950

FOREIGN PATENTS

589,966	Great Britain	July 4, 1947