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54 **Method to obtain coatings on mechanical parts by P/M techniques.**

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**DE-B- 1 185 901**  
**US-A- 4 371 589**  
**US-A- 4 626 406**

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## Description

This invention applies to a method to obtain coatings on mechanical parts by P/M (Powder Metallurgy) techniques by means of a paste which is applied on the substrate part surface, the paste being formed by a binder and by metallic and/or ceramic powders, the operations being carried out by adding an additive to the paste at atmospheric pressure and temperature ranging between 10 and 500 C; homogeneizing the resulting paste mixture and additive by mechanical agitation at atmospheric pressure or applying vacuum for a period ranging 3 and 60 minutes and applying the product obtained this way on the substrate part to coat in any known way.

Powder Metallurgy offers unique advantages, as for instance to obtain materials composed by a metallic matrix with non metallic inclusion or self-lubricating materials with oil containing porosity. For this and other reasons, several P/M methods have been developed to obtain coatings on substrate parts.

The most common method to apply coatings on substrate parts is the single-axis pressing of two powder layers of different composition which form parts composed by two different materials after sintering. The limit in this case is the impossibility of filling a die and densifying powders over non flat surfaces, for instance on spherical and conical surfaces.

Another application method is the injection moulding of a plastified mixture in a cavity where the substrate part is an insert or part of the mould. This method is especially suitable to large series.

A paste like product can be also applied by forming a sheet from which shapes are cut and stuck to the substrate part.

In fact, coatings can be obtained by any method for paste application, as for instance a brush, smoother, centrifugation etc.

Several methods are known to obtain a paste composed of a binder and metallic or ceramic powders or mixtures of both, as for example the methods described in article 5 of the publication "Progress in Powder Metallurgy" volume 42, 1986.

The binder ratio varies according to the powder grain size or according to the specific powder surface. The binder may be of wax basis, being formed, for instance, by wax and petrolatum or of polymeric basis, being formed, for instance by polymethylmetacrylate dissolved in toluene or of water based, formed, for instance, by a solution of cellulosic glue or by a combination of various.

The materials of the substrate part have only the limitation of being compatible with the temperature and atmosphere used when sintering the coating.

The pastes may be also used for manufacturing parts without substrate, i.e. totally formed by the coating material, by means of coating a substrate of the required shape and detachable after sintering, as for instance graphite.

Binder forming always comprises a thermal treatment stage for binder removal before sintering the powders. This stage is the most critical of the process, since faults easily appear, as for instance distortion of the part shape of cracks and craters on the surface. To avoid these defaults a very slow warmup and a very long process duration are necessary, resulting in a high cost, and consequently in a necessary limitation of the process to very specific applications.

It is obvious that the binder composition influences the shaping properties of the paste and the coating behaviour during thermal treatment.

Pastes based on wax are very plastic at room temperature, consequently they are easily formable. However, as the temperature increases, its viscosity reduces and, therefore, they tend to flow and distort during the removal stage.

Pastes based on cellulose or water solved polysaccharides harden with temperature and retain well the shape during binder removal, but they have poor formability and its viscosity at room temperature is very affected by solvent losses during storage or handling.

Thermoplastic polymers with solvents also harden when heating and solvent evaporation, but they soften again when temperature further increases. They are easily conformable, but they are affected by distortion during removal and variable viscosity with solvent losses.

The known processes use to combine the mentioned basic compositions, for instance a wax with one polymer and one solvent or plasticizer in order to compensate advantages and disadvantages. Besides, all known pastes require slow heating, as we already stated, to avoid internal pressures by vapors or decomposition gases caught inside the pastes which generate craters and cracks when reaching the surface.

The minimum temperature to assure total removal of a organic type binder is 5000 C and the most favorable atmosphere is oxidant. The total process with usual heating speeds of 0,50 C per minute has a duration of 9 to 10 hours and results in very rusty parts. This oxidation is used to furnish a cementing skeleton among the particles as the binder is disappearing. However, it is negative for the sintering stage in major or minor degree, according to the alloy elements, since the oxide reduction requires high temperatures and longer exposure times to reducing atmospheres. In addition, the dimensional change in sintering depends upon the oxidation degree and in the case of bronzes

very much.

As it has already been seen, coatings of this type need a slow heating speed at the critical binder removal stage. In order to avoid distortions, cracks or craters coatings are very thin (between 10 and 50 microns) or they are conceived for very concret applications, as for instance the coating described in the US Patent No. 4.596.692 from Morishita and others, or they use a specific and concret binder as mentioned in the US Patent No. 4.491.559 from Kennametal Inc. which contains metal particles of tungsten carbide.

As already stated parts can be entirely made from pastes suitable for coatings, as those manufactured according to the US Patent No. 4.626.406 from Inco Alloys International Inc. which discloses a process for the activated sintering of metallic powders. In this process a slurry is produced by mixing a metal powder, a binder (a hydroxyethyl cellulose polymer), water and an additive consisting of an aqueous solution of boric acid. The slurry is introduced into a forming apparatus and formed into a desired shaped object. The object is heated to remove the binder and then sintered. The slurries of DI are prepared by mixing the dry components and then adding the boric acid solution to form a clay like slurry. The boric acid solution is prepared by dissolving boric acid in warm (49°C) distilled water. The slurry is extruded into a rod and air dried for about 48 hours and subsequently the rod is heated to 482°C to remove the binder and then sintered at 1316°C. However, these pastes present a serious obstacle consisting in the binder removal stage which must be carried out by a very slow temperature increase taking days and in some cases even weeks. Therefore, in such cases it is a question of very concret application processes.

Surprisingly it has been found out that the method subject to this invention allows coatings which admit a fast temperature increase from the moment of removing the water based vehicle or the polar solvent without outflow nor distortion after the binder removal has been finished. The coating obtained according to the method subject of this invention shows an excellent homogeneity and after debinding a suitable strength for handling on trays, pallets and trucks without more care than usual in manufacturing plants. Coating pastes obtained according to this invention allow fast heating from 120°C approximately and without shape distortions, cracks or craters and in a reducing, neutral or oxidant atmosphere and even in vacuum.

Basically the coating accordingly the invention allows shorter debinding and is more flexible on alloy elements oxygen affinity than the methods known until now.

Essentially the method according to the invention is characterized in that said additive is formed

by a solution, in a polar solvent, of free or complex metallic ions and in that after said coating of the substrate part the operations are carried out of performing a first binder removal stage by application of heat to a temperature of about 120°C, at a rate of temperature increase of about 0.5°C per minute, to remove the polar solvent and performing a second binder removal stage by heating at a higher rate of temperature increase than used in the first binder removal stage to remove the binder, the part then being ready to be submitted to the known sintering and finishing operations.

According to another invention feature, the mentioned additive is chosen among those which do not produce precipitates at atmospheric pressure below 80°C. They precipitate between 80 and 120°C and their precipitates are stable below 200°C.

According to another invention feature, the mentioned additive is chosen in such a way that its free metallic ions are compatible with the metallic and/or ceramic powders used to make the paste.

In order to better clarify the invention below three examples of realization of the method are given:

#### EXAMPLE 1:

Spherical bronze 70 % Sn, particle size ranging between 250 and 125 microns was mixed with a binder formed by 80% petrolatum and 20% of Hoechst wax type C in a proportion of 93% powder and 7% binder. This paste was applied on a cylindrical surface of P/M steel parts 2% copper, density 6.8 g/cc, forming a 1.2 mm thickness. Then binder cycles were tested in an oven with air atmosphere with different heating speeds. In this way the cycle represented in figure 1, curve a, was determined as the shortest and still free of distortions and cracking. An identical paste to the previous one was prepared but adding 2% of an additive formed by 17% of copper sulphate and 83% of water. Tests to determine the shortest cycle were performed and the cycle represented in figure 1, curve b, was obtained. It is noted that the presence of the additive according to this patent allows the reduction of binder removal practically to half the time.

#### EXAMPLE 2:

A mixture of atomized iron powder with particle size below 100 microns and atomized nickel powder with particle size below 50 microns in a proportion of 96% iron and 4% nickel was prepared. This mixture was then mixed with a binder formed by 80% petrolatum and 20% Hoechst wax type V in a proportion of 90% to 10%. The obtained paste was

conformed as in the previous examples and submitted to removal cycles producing in all cases a coating overflow. To this paste was added 1% of an additive formed by 40% in weight of iron ammoniac oxalate and 60% water.

The parts coated with this additivated paste were submitted to a removal cycle represented in figure 1, curve b, without producing distortions, cracking nor craters.

#### EXAMPLE 3:

Spherical bronze 90% Cu-10% Sn with a particle size ranging between 300 and 100 microns was mixed with a binder formed by 58,3% in petrolatum, 1,8% in weight of sodium alginate and 39,9% of water in a proportion of 85% powder and 15% binder. This paste was applied on the cylindrical surface of test parts with 1.5 mm thickness. By the same methodology of example 1, the thermal cycle represented in figure 1, curve a, was determined as the shortest to avoid cracks. In the same test a paste identical to the previous one was prepared but by adding 1.5% of an additive formed by 17% in weight of copper sulphate and 83% of water. In the test to determine the shortest cycle, the cycle represented in figure 1, curve b, was obtained. Once again the presence of additive allows reducing the removal time.

#### Claims

1. Method to prepare coatings by P/M (Powder Metallurgy) techniques on mechanical parts by means of a paste which is applied on the substrate part surface, the paste being formed by a binder and by metallic and/or ceramic powders, the operations being carried out of adding an additive to the paste at atmospheric pressure and temperature ranging between 10 and 50°C; homogeneizing the resulting paste mixture and additive by mechanical agitation at atmospheric pressure or applying vacuum for a period ranging 3 and 60 minutes and applying the product obtained this way on the substrate part to coat in any known way, characterized in that said additive is formed by a solution, in a polar solvent, of free or complex metallic ions and in that after said coating of the substrate part the operations are carried out of performing a first binder removal stage by application of heat to a temperature of about 120°C, at a rate of temperature increase of about 0.5°C per minute, to remove the polar solvent and performing a second binder removal stage by heating at a higher rate of temperature increase than used in the first binder removal stage to remove the binder, the part then being

ready to be submitted to the known sintering and finishing operations.

2. Method to prepare coatings according to claim 1, characterized in that the mentioned additive is chosen among those which do not produce precipitates at atmospheric pressure below 80°C; they precipitate between 80 and 120°C; and their precipitates are stable below 200°C.
3. Method to prepare coatings according to claims 1 and 2 characterized in that the mentioned additive is chosen in such a way that its free metallic ions are compatible with the metallic and/or ceramic powders used to make the paste.

#### Patentansprüche

1. Verfahren zur Herstellung von Beschichtungen bei pulvermetallurgischen Verfahren an mechanischen Teilen mit einer Masse, die auf die Substratteiloberfläche aufgetragen wird. Die Masse wird aus einem Bindemittel und einem Metall- bzw. Keramikpulver gebildet. Die Arbeitsgänge umfassen das Beimischen eines Zusatzstoffes in die Masse bei atmosphärischem Druck und einer Temperatur zwischen 10 und 50 Grad C. Die entstehende Massemischung und der Zusatzstoff werden durch mechanisches Rühren bei atmosphärischem Druck bzw. bei Anwendung von Vakuums 3 bis 60 Minuten lang homogenisiert. Das so erzielte Erzeugnis wird auf das zu beschichtende Substratteil aufgetragen. Der besagte Zusatzstoff wird durch ein polares Lösungsmittel aus freien bzw. komplexe Metallionen gebildet. Nach der besagten Beschichtung des Substratteils werden weitere Arbeitsgänge durchgeführt, indem zunächst eine Bindemittelbeseitigung durch Anwendung von Hitze bei einer Temperatur bis ca. 120 Grad C und einer Temperaturzunahmegeschwindigkeit von ca. 0,5 Grad C pro Minute zur Beseitigung des polaren Lösungsmittels und durch Anwendung einer zweiten Bindemittelbeseitigungsphase durch Erhitzung bei einer höheren Temperaturzunahmegeschwindigkeit als in der ersten Bindemittelbeseitigungsphase erfolgt. Anschliessend ist das Teil fertig zum Sintern und zur Fertigbearbeitung.
2. Verfahren zur Herstellung von Beschichtungen gemäss Patentanspruch 1. Es ist gekennzeichnet durch die Auswahl des erwähnten Zusatzmittels aus solchen Zusatzmitteln, die keine Ablagerungen bei atmosphärischem Druck un-

ter 80 Grad C bilden. Sie lagern sich ab zwischen 80 und 120 Grad C. Die Ablagerungen sind unter 200 Grad C beständig.

poudres métalliques et/ou céramiques utilisés dans la preparation de la pâte.

3. Verfahren zur Herstellung von Beschichtungen gemäss Patentansprüche 1 und 2, welches dadurch gekennzeichnet ist, dass das gesamte Zusatzmittel so gewählt wird, dass dessen freie Metallionen mit dem zur Herstellung der Masse eingesetzten Metall- und/oder Keramikpulver vereinbar sind. 5  
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### Revendications

1. Méthode pour l'obtention de couches par techniques de la métallurgie des poudres sur des pièces mécaniques par le moyen d'une pâte qui est appliquée sur la pièce substrat, la pâte étant composée d'un liant et de poudres métalliques ou céramiques, avec la réalisation des opérations d'ajouter un additif à la pâte à la pression atmosphérique et à température entre 10 et 50 degrés centigrades; d'homogénéiser le mélange de la pâte et de l'additif par agitation mécanique à la pression atmosphérique ou avec du vide, pendant un période entre 3 et 60 minutes et d'appliquer le produit obtenu de cette façon sur la pièce substrat à recouvrir par n'importe quelle procédure connue; caractérisé par ce que l'additif cité est obtenu par solution dans un solvant polaire des ions métalliques libres ou complexes et par ce que après l'application de la couche sur la pièce substrat on fait les opérations d'une première étape d'élimination du liant par application de chaleur jusqu'à près 120 degrés centigrade et avec une vitesse de croissance de la température proche de 0,5 degrés centigrade par minute pour éliminer le solvant polaire et d'une deuxième étape avec une vitesse de croissance plus élevée que celle utilisée dans la première étape, avec le résultat de que la couche devienne prête pour les opérations connues de frittage et finissage. 15  
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2. Méthode pour l'obtention de couches suivant la revendication 1 caractérisée par ce que l'additif cité est choisi entre ceux qui ne produisent pas des précipités à la pression atmosphérique par dessous de 80 degrés centigrade, ils précipitent entre 80 et 120 degrés centigrade et ces précipités sont estables par dessous 200 degrés centigrades. 50
3. Méthode pour l'obtention de couches suivant les revendications 1 et 2 caractérisée par ce que l'additif cité est choisi de façon que les ions métalliques libres soient compatibles avec les 55

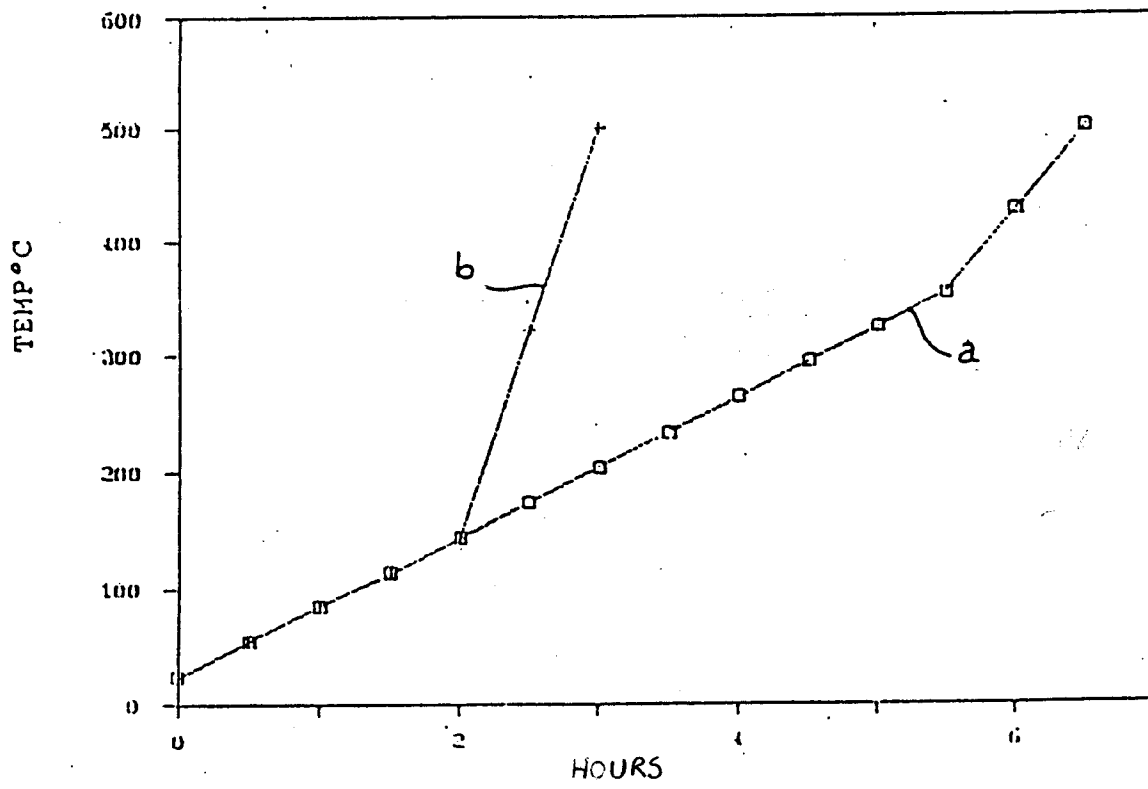


FIG. 1