

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

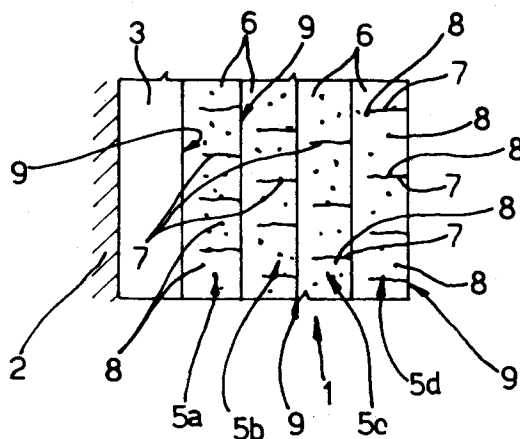
0 668 375 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **95102258.1**(51) Int. Cl.⁶: **C25D 15/02**(22) Date of filing: **17.02.95**(30) Priority: **18.02.94 IT TO940101**(43) Date of publication of application:
23.08.95 Bulletin 95/34(84) Designated Contracting States:
DE GB NL(71) Applicant: **INDUSTRIALE S.r.l.**
Via San Ouirico, 19
I-16121 Genova (IT)(72) Inventor: **Capezzuoli, Giulio**
Via S. Ouirico, 19
I-16163 Genova (IT)(74) Representative: **Plebani, Rinaldo et al**
c/o Studio Torta,
Via Viotti 9
I-10121 Torino (IT)

(54) **Process for forming composite galvanic coatings of hard chromium with a disperse phase, and wear-resistant coating formed thereby.**

(57) A process applicable to components subjected to chafing, such as internal combustion engine piston rings and similar, and wherein, after preferably first depositing a first continuous galvanic layer of Cr in a conventional bath, at least a second layer of Cr is deposited galvanically in a chromium plating bath in which is dispersed a predetermined concentration of 0.1-20 μm particles of a nonmetal insoluble in the bath, and using a pulsating cathode current varying cyclically in time between a minimum and maximum value, so that the second Cr layer presents microcracks with a predetermined distribution, and the nonmetal particles are included partly inside and partly outside the microcracks, while at the same time limiting inclusion in the layer of the hydrogen developed in the bath.

**Fig.1****EP 0 668 375 A1**

The present invention relates to a process for forming, on a substrate, a composite hard chromium coating comprising a disperse phase consisting of nonmetal particles; and to a wear-resistant coating formed using such a process and particularly suitable for mechanical components subjected to high-temperature chafing, such as internal combustion engine piston rings and components.

US Patent n. 4,846,940 relates to galvanic hard chromium coatings characterized by a Cr matrix with a large number of micro- and macrocracks combined with a disperse phase, in the matrix, consisting of hard particles embedded in the micro- and macrocracks of the matrix. Such coatings are formed by means of a galvanic electrodeposition process characterized by comprising a current inversion step, i.e. by alternately switching the substrate from cathode to anode potential and vice versa.

Such coatings present a small amount of incorporated hydrogen, a large number of even relatively large cracks, and a large number of particle inclusions in the cracks, which make them highly susceptible to corrosion. Moreover, depositing the coating by inverting the polarity of the electrodes poses practical problems which complicate the fabrication process.

It is an object of the present invention to provide a process for forming hard chromium coatings comprising at least one layer with a microcracked matrix and a disperse phase, and which is both straightforward and economical while at the same time providing for good quality coatings characterized by a small amount of incorporated hydrogen. It is a further object of the present invention to provide a composite hard chromium coating of good quality and strength, which remains extremely hard even at high temperature, and which is highly resistant to corrosion and wear both of itself and the mating part.

According to the present invention, there is provided a process for forming, on a substrate, a composite hard chromium coating comprising a disperse phase and particularly suitable for mechanical components subjected to high-temperature chafing; the process comprising the step of galvanically depositing at least one layer of hard chromium in a chromium plating bath of the type forming microcracks and in which is dispersed in suspension a predetermined concentration of given sized particles of a nonmetal insoluble in the bath;

characterized in that, in the course of said deposition step, the substrate is maintained permanently at cathode potential; and a pulsating cathode current, varying cyclically in time between a minimum and maximum value, is supplied to achieve a chromium layer comprising a matrix with microcracks of a given distribution, and a disperse phase consisting of said nonmetal particles, some of which are included in the microcracks, and some of which are directly embedded in the matrix.

This provides for achieving a so-called "disperse chromium" coating comprising a Cr matrix containing dispersing agents, which is extremely hard (over 1,000 Vickers), includes dispersing agents in the form of nonmetal particles of hard materials such as oxides, carbides and nitrides of very low thermal conductivity and high thermal stability, and which, combined with a low hydrogen content, presents a high degree of thermal stability characterized by a reduced loss in hardness alongside an increase in temperature, and a small amount of incorporated hydrogen in the Cr matrix. Moreover, variation of the cathode current may be achieved easily using known facilities, and fully automatically by means of appropriate programming, thus enabling troublefree, low-cost formation of the coating according to the present invention.

The above deposition step is preferably preceded by the step of depositing on the substrate a continuous hard chromium base layer with substantially no microcracks or porosity, which covers the whole of the substrate, and which is formed, preferably to a thickness of roughly 50 μm , by galvanically depositing chromium in a chromium plating bath of the type forming no microcracks and containing no particles in suspension. A number of said "disperse" layers comprising a microcracked Cr matrix and including hard particles are then deposited successively on the continuous base layer.

The substrate-coating interface thus presents a fairly thick layer (in relation to the total thickness of the coating, which is roughly 500 μm) with absolutely no cracks or dispersing agent particles (at least none detectable by standard metallographic techniques), and which prevents the microcracks in the upper layers of the coating from propagating towards the substrate, thus ensuring absolute protection of the substrate and greatly enhancing the corrosion resistance of both the substrate and the coating.

When galvanically depositing each said hard chromium layer comprising a microcracked matrix and a disperse phase consisting of said particles embedded in the layer, the cathode current is supplied according to a cycle comprising the following steps:

- a first step wherein the cathode current is brought to and maintained for a first predetermined time at a first threshold value other than zero;
- a second step, superimposed on the first, wherein the cathode current is varied alternately, in a wave pattern and for a second predetermined time, between said first threshold value and a second threshold value higher than the first; and

- a third step wherein the cathode current is zeroed and maintained at zero for a third predetermined time.

More specifically, in said second step, the cathode current is varied in a square wave pattern; and in said first and third steps, it is varied in steps.

5 The "disperse chromium" layers are therefore formed with the microcracks of one layer offset, depthwise of the coating, in relation to those of the adjacent "disperse" layers, so that any depthwise propagation of the microcracks in one layer (due to mechanical stress in the layer) is prevented from being transmitted to those of the adjacent underlying layer, thus preventing the formation of macrocracks as in galvanic Cr coatings formed using known processes. This provides for obtaining a much more stable
10 coating, and for further improving the corrosion resistance of the substrate, without, however, affecting the in-service lubricant collecting and distribution function of the microcracks.

Finally, the presence of nonmetal dispersing agent particles substantially consisting of oxides (e.g. aluminium oxide - Al_2O_3) and/or carbides (tungsten, chromium, silicon, boron) and/or nitrides (silicon, boron), i.e. extremely hard compounds, and both included inside the microcracks and embedded directly in
15 the chromium matrix, provides for obtaining a coating which is extremely resistant to wear caused by abrasion or adhesion typical of high-temperature, mutually sliding metal surfaces.

The coating according to the present invention therefore comprises a layer comprising a microcracked hard chromium matrix and a disperse phase, in the matrix, consisting of a number of particles of a nonmetal material, and is characterized by a first number of said particles being included in the microcracks of the
20 matrix, and by a second number of said particles being embedded directly in parts of the matrix with no microcracks. More specifically, the wear-resistant coating according to the present invention comprises a first hard chromium layer with substantially no microcracks or porosity and without said particles; and, deposited on the first layer, a number of said layers comprising a microcracked matrix and a disperse phase consisting of said particles; the first layer presenting a thickness of at least 50 μm ; the superimposed
25 layers, deposited on the first layer, presenting the microcracks offset depthwise in relation to those of the adjacent layers; the width of the microcracks, measured parallel to the layer, being at least 1 μm ; the density of the microcracks ranging from 100 to 300 per centimeter; and the size of the nonmetal particles embedded in the matrix ranging from 0.1 to 20 μm .

The favourable tribological properties of such coatings make them particularly suitable for sliding
30 components cooperating with cylinder liners, such as the piston rings of four- and two-stroke engines or piston pumps, wherein the cylinder liners are normally made of lamellar, nodular or vermicular cast iron, either natural or hardened (e.g. laser quenched) or nitrided (e.g. using the TENIFER (registered trade mark) process or similar), or present surfaces with hot spray coatings such as FK1008 formed using the HVOF process (both registered trade marks).

35 A number of non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying Figures, in which:

Figure 1 shows a schematic section, perpendicular to the surface extension, i.e. in the direction of the thickness, of a coating in accordance with the present invention;

Figure 2 shows a hardness graph of different materials as a function of temperature;

40 Figures 3, 4 and 5 show microphotographs of galvanic coatings formed using the process according to the present invention;

Figure 6 shows a graph of a spot EDS analysis of the Cr matrix of a coating in accordance with the present invention.

Number 1 in Figure 1 indicates a wear-resistant coating formed according to the present invention on a
45 substrate 2, e.g. any known mechanical component made of cast iron. Coating 1 comprises a first layer 3, preferably no more than 50 μm deep, formed of hard Cr, and characterized by being continuous, i.e. by presenting no detectable microcracks or porosity, and no inclusions of any sort. On top of layer 3, there are deposited a given number (four in the example) of substantially identical layers 5a, 5b, 5c, 5d, each comprising a hard chromium matrix 6 in which are formed a number of microcracks 7 extending radially
50 depthwise of layer 5 towards substrate 2, and a disperse phase in matrix 6 and consisting of a number of particles 8 of any hard nonmetal material.

According to the present invention, and as shown clearly, albeit schematically, in Figure 1, a first number of particles 8 is included in microcracks 7 of matrix 6, and a second number of particles 8 is embedded directly inside parts of matrix 6 with no microcracks 7; and the microcracks 7 of layers 5
55 deposited on first layer 3 are offset depthwise in relation to those of the adjacent layers 5. For example, as shown in the Figure 1 section, microcracks 7 of layer 5b extend depthwise towards underlying layer 5a and substantially towards the portions between microcracks 7 of layer 5a, i.e. towards matrix 6 portions of layer 5a presenting no microcracks. When viewed from above, the microcracks 7 of each layer 5 present a

"spiderweb" pattern along the interface surface 9 of each layer 5, as shown in Figure 5.

According to the present invention, the width of the microcracks, measured parallel to each layer 5, is at least 1 μm ; the microcrack density measured at surfaces 9 ranges from 100 to 300 microcracks per centimeter of surface; and the size of nonmetal particles 8 ranges from 0.1 to 20 μm .

According to the present invention, a coating as described above may be formed electrolytically; layer 3 being formed by galvanically depositing Cr in known manner using any known chromium plating bath of the type resulting in no microcracks and containing no particles in suspension, or operating accordingly with a bath containing particles in suspension; and layers 5 being formed using known chromium plating baths of the type for forming microcracks and containing particles 8 in suspension. A further precaution to ensure layer 3 presents no microcracks is to limit its thickness, and to use such operating parameters (current cycles and density, etc.) as to limit the formation of stress within the layer due to excessive energy supply.

According to the present invention, to achieve the above characteristics of layers 5 (particles 8 included both inside the microcracks and directly in the matrix, and microcracks offset between one layer and another), when depositing the layer on to the substrate (or underlying layer 5), substrate 2 is maintained permanently at cathode potential, and a pulsating cathode current varying cyclically in time between a minimum and maximum value is supplied. Also, the baths for forming layers 5 and containing particles 8 in suspension are preferably agitated at all times, e.g. by means of mechanical, fluidodynamics, energetic agitators, or by air injection.

The nonmetal particles 8 included in the coating must be insoluble in the baths which present a chromic acid, sulphuric acid and catalyst base, are maintained at a temperature of about 55 °C, and present a 20 to 400 gr/liter concentration of particles 8 (ranging in size between 0.1 and 20 micron). Particles 8 therefore consist of one or more materials in the group comprising: tungsten carbide, silicon carbide, chromium carbide, aluminium oxide, silicon nitride, boron carbide, diamond, graphite, hexagonal boron nitride. Each layer 5 may of course include particles 8 all of the same material or of different materials, and likewise from one layer to another.

The cathode current supply cycle comprises the following steps:

- a first step wherein the cathode current is increased in steps to a first threshold value other than zero (roughly 70 amps per square decimeter) and maintained at that value for a first predetermined time ranging from 10 to 60 seconds;
- a second step, superimposed on the first, wherein the cathode current is varied alternately, in a square wave pattern, between the first threshold value and a second threshold value higher than the first; in particular, using a pulse amplitude of 0.2-0.5 times the first threshold value, i.e. $0.2-0.5 \times 70 = 14-35 \text{ A/dm}^2$, and an oscillation period of 0.01 to 1 second; and for a time ranging from 10 to 60 seconds;
- a third step wherein the cathode current is zeroed in steps and maintained at zero for a third predetermined time ranging from 0.03 to 60 seconds.

The following is a non-limiting embodiment by way of example of the present invention.

EXAMPLE

Using a 1500 lt tank, a bath with the following composition is prepared:

CrO ₃	250.0 gr/lt;	FeSiF ₆	1.5 gr/lt;
H ₂ SO ₄	2.5 gr/lt	SiC (*)	50.0 gr/lt;

(*) particle size: 50% of 2.5 μm

Lead anodes and a cathode consisting of rings of lamellar cast iron are immersed in the bath, and a chromium coating is deposited, agitating the bath by recirculating roughly 300 lt/min and injecting air at roughly 5 bar pressure, and operating with a potential difference of 15 volts and a continuous cathode current of a mean density of 70 A per square decimeter, which is varied during deposition according to the following cycle:

- a first step wherein the cathode current is increased in steps from zero to 70 A/dm² and maintained at that value for 20 seconds;
- a second step, superimposed on the first, wherein the cathode current is oscillated in a square wave pattern with a bandwidth of 18 A/dm² and a frequency of 16 Hz for the same time of 20 seconds;
- a third step wherein the cathode current is zeroed in steps and maintained at zero for 0.03 seconds;
- repetition of the cycle from the beginning.

This eventually produces the coating shown in the Figure 4 section, which presents excellent adherence at the coating-substrate interface. The Figure 3 photograph (enlarged 625 times) of the unetched coating, and the similar top plan view in Figure 5 show the characteristics of the coating: good adherence, low microcrack density, and inclusion of silicon carbide particles both inside and outside the cracks. This is confirmed by EDS analysis (Figure 6) of specimen pieces, which shows the typical Cr and Si peaks of a spot analysis of the matrix far from the cracks.

Claims

1. A process for forming, on a substrate, a composite hard chromium coating comprising a disperse phase and particularly suitable for mechanical components subjected to high-temperature chafing; the process comprising the step of galvanically depositing at least one layer of hard chromium in a chromium plating bath of the type forming microcracks and in which is dispersed in suspension a predetermined concentration of given sized particles of a nonmetal insoluble in the bath;
characterized in that, in the course of said deposition step, the substrate is maintained permanently at cathode potential; and a pulsating cathode current, varying cyclically in time between a minimum and maximum value, is supplied to achieve a chromium layer comprising a matrix with microcracks of a given distribution, and a disperse phase consisting of said nonmetal particles, some of which are included in the microcracks, and some of which are directly embedded in the matrix.
2. A process as claimed in Claim 1, characterized in that said deposition step is preceded by the step of depositing on the substrate a continuous hard chromium base layer with substantially no microcracks or porosity and which covers the whole of the substrate; said base layer being formed by galvanically depositing chromium in a chromium plating bath of the type forming no microcracks.
3. A process as claimed in Claim 2, characterized in that, on said base layer, there are deposited galvanically a number of said hard chromium layers, each comprising a microcracked matrix and a disperse phase; said layers being so formed that the microcracks of each layer are offset depthwise in relation to the microcracks of the adjacent layers.
4. A process as claimed in one of the foregoing Claims, characterized in that said nonmetal particles insoluble in the bath consist of one or more materials in the group comprising: tungsten carbide, silicon carbide, chromium carbide, aluminium oxide, silicon nitride, boron carbide, diamond, graphite, and hexagonal boron nitride.
5. A process as claimed in one of the foregoing Claims, characterized in that, during the step of galvanically depositing each said hard chromium layer comprising a microcracked matrix and a disperse phase consisting of said particles embedded in the layer, the cathode current is supplied in a cycle comprising the following steps:
 - a first step wherein the cathode current is brought to and maintained for a first predetermined time at a first threshold value other than zero;
 - a second step, superimposed on the first, wherein the cathode current is varied alternately, in a wave pattern and for a second predetermined time, between said first threshold value and a second threshold value higher than the first; and
 - a third step wherein the cathode current is zeroed and maintained at zero for a third predetermined time.
6. A process as claimed in Claim 5, characterized in that, in said second step, the cathode current is varied in a square wave pattern; and in said first and third steps, the cathode current is varied in steps.
7. A wear-resistant hard chromium coating, characterized in that it is formed using the process as claimed in one of the foregoing Claims from 1 to 6.
8. A wear-resistant hard chromium coating formed electrolytically, comprising a layer in turn comprising a microcracked hard chromium matrix and a disperse phase, in the matrix, consisting of a number of particles of a nonmetal material, and particularly suitable for mechanical components subjected to high-temperature chafing; characterized in that a first number of said particles is included in the microcracks of the matrix, and a second number of said particles is embedded directly in parts of the matrix with no

microcracks.

9. A wear-resistant hard chromium coating as claimed in Claim 8, characterized in that it comprises a first hard chromium layer with substantially no microcracks or porosity and without said particles; and, deposited on said first layer, a number of said layers comprising a microcracked matrix and a disperse phase consisting of said particles; the first layer presenting a thickness of at least 50 μm ; and the microcracks of said layers deposited on the first layer being offset depthwise in relation to the microcracks of the adjacent layers.
10. A wear-resistant hard chromium coating as claimed in Claim 8 or 9, characterized in that the width of the microcracks, measured parallel to the layer, is at least 1 μm ; the density of the microcracks ranges from 100 to 300 microcracks per centimeter; and the size of said nonmetal particles ranges from 0.1 to 20 μm .

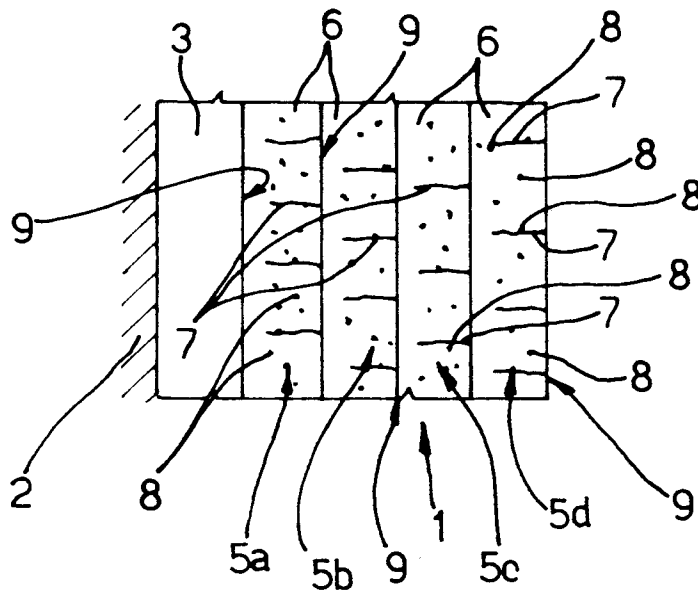


Fig.1

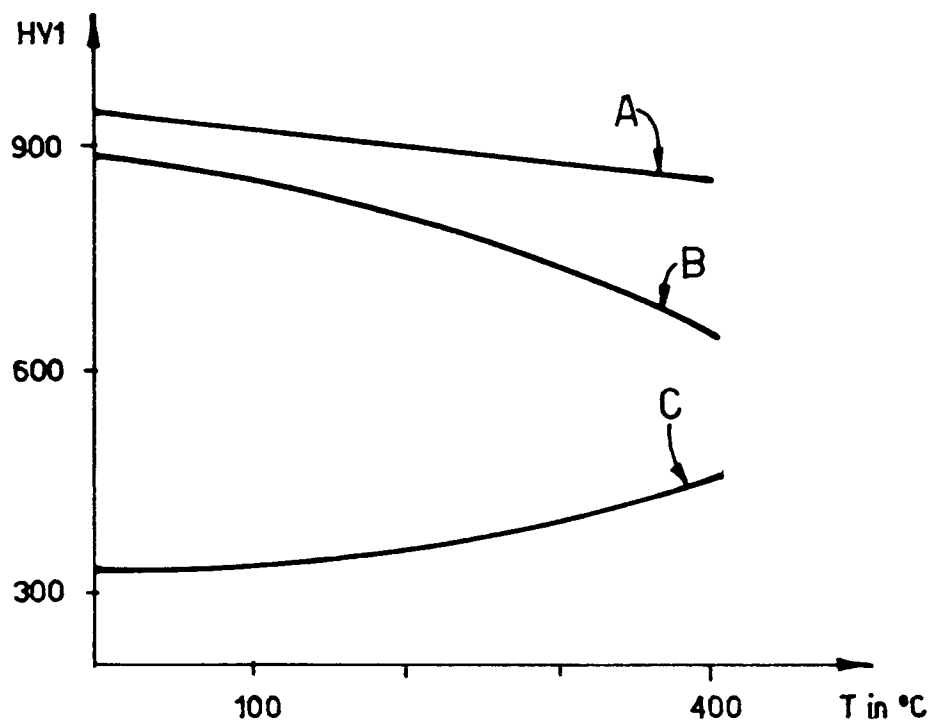


Fig.2

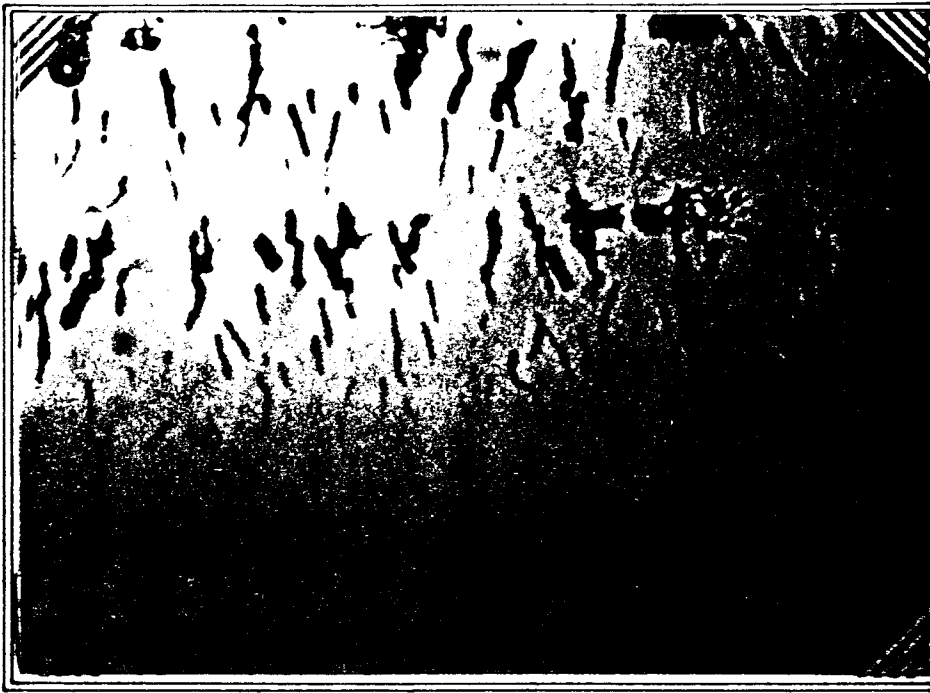
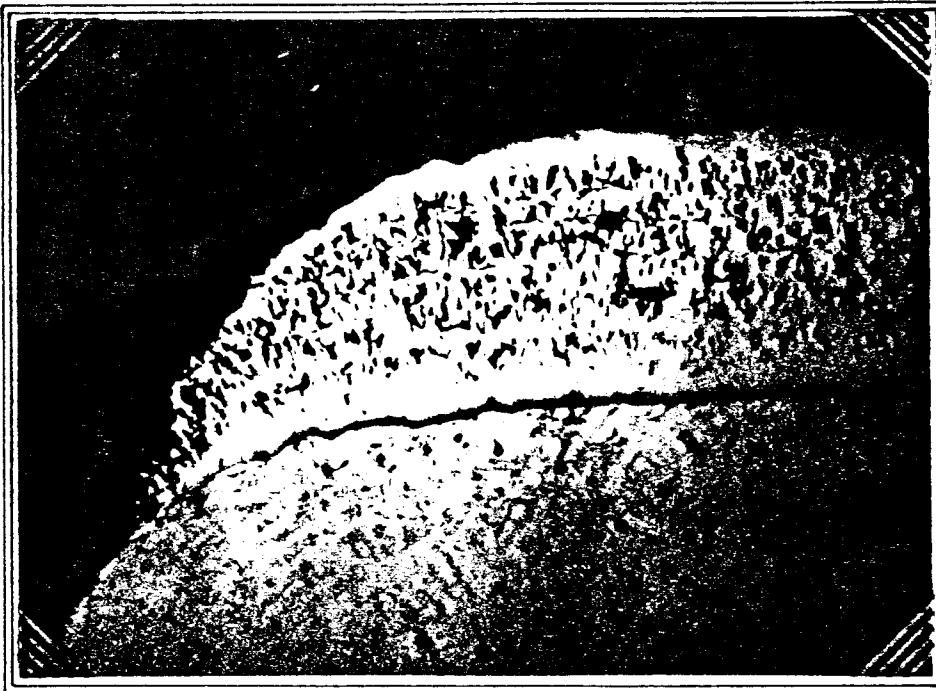


Fig. 3



GG

Fig. 4

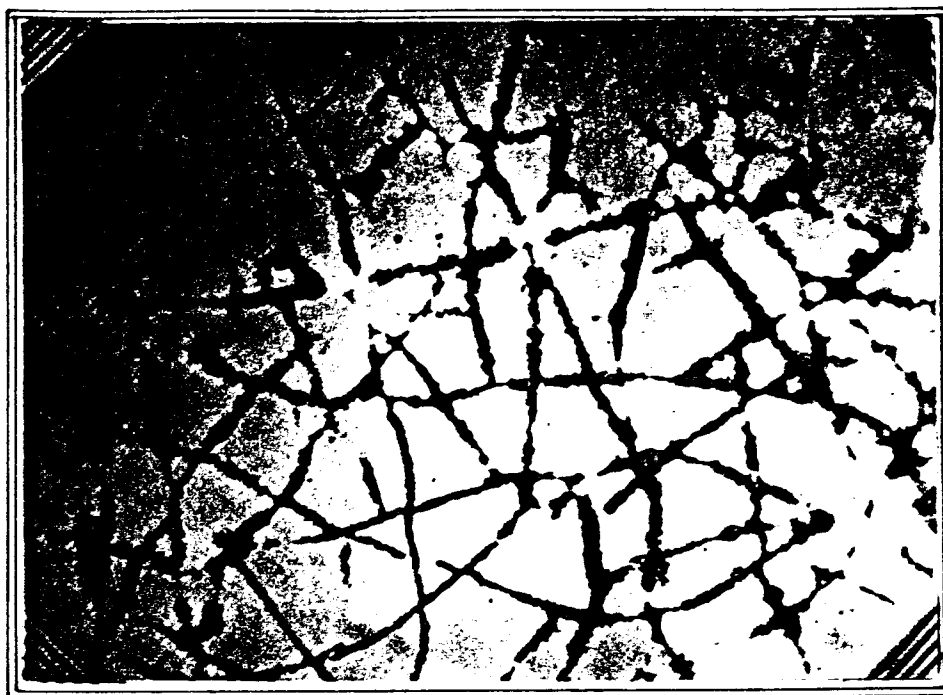


Fig. 5

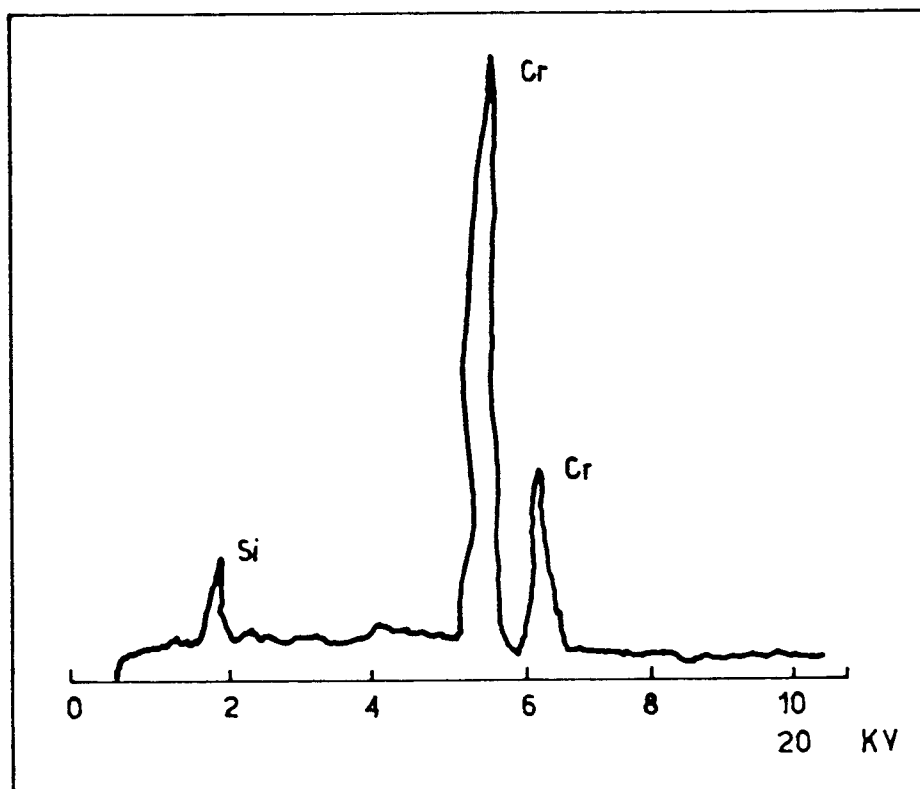


Fig. 6



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 10 2258

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A,D	EP-A-0 217 126 (GOETZE AG) ---		C25D15/02
A	DE-A-39 33 896 (LPW-CHEMIE GMBH) * page 5; claim 6 *		
A	---		
	PLATING & SURFACE FINISHING, vol.74, no.9, September 1987, USA pages 70 - 72 TAKAYA 'trivalent chromium composite coatings containing silicon carbide or diamond particles' * page 72, column 1, line 6 - line 9 * -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C25D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 April 1995	Examiner Nguyen The Nghiep, N
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			