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## (54) A process and an equipment to form a sulphide case at the surfaces of metal parts.

(57) The present invention relates to a process and the corresponding equipment, with which a case of sulphide forms at the surface of metal part (5) by heating and gasifying sulphur, the metal part (5) is on the table (4) of cathode in a vacuum reacting chamber (1) of said equipment while a vapourizer - (6) is provided in the same vacuum reacting chamber (1), the vapourizer (6) being heated with a low voltage supply (11) and used to hold solid sulphur. Under vacuum condition, solid sulphur will be gasified by heating and the gasified sulphur will be ionized and discharged with glow under the action of a direct electric field at high voltage between the anode (2) and cathode (4), under the glow discharge conditions, the positive sulphur ions will bombard the metal parts (5) which are located on the cathode table (4) and a sulphide case will be formed at the surfaces of parts (5).

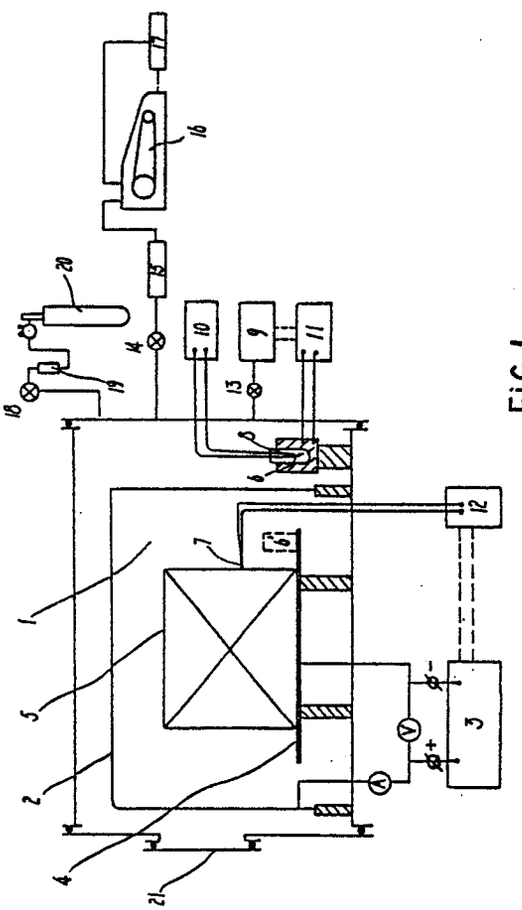


FIG.1

EP 0 218 916 A1

# A PROCESS AND AN EQUIPMENT TO FORM A SULPHIDE CASE AT THE SURFACES OF METAL PARTS

The present invention relates to a process and an equipment to form a sulphide case at the surfaces of metal parts, more particularly, relates to such a process and an equipment that are used to form a sulphide case at the surfaces of the metal parts by means of gas sulphurizing.

Sulphurizing is one of the surface-treating procedures for metal parts. Since a ferrous sulphide case can be formed by sulphurizing, and ferrous sulphide is a kind of solid lubricant, therefore if there is a sulphide case between two contacting surfaces of friction parts, the friction coefficient may be decreased. Furthermore, a sulphide case may separate the basic metal of two friction parts from direct contact with each other, and thereby the surface of part provides fine resistance to wear and to seizure. Therefore recent years the study on sulphurizing has been further developed and paid a great attention to.

It is known that the solid and liquid sulphurizing have been studied but both still have some disadvantages such as long processing duration, great energy consumption, unstable sulphurizing quality and less depth of sulphurized case. From then a new gas sulphurizing technology-low temperature electrolytical sulphurizing has been developed. The technology has been developed rapidly because it features a low treating temperature, less deformation and being able to carry on the processing after the traditional processes such as carburizing, nitriding, low-temperature temper and induction heating-quenching.

There was a paper issued at the seminar of IFHT in 1978. The paper introduced a gas-sulphurizing process by means of nitrosulphurizing. Although with this process, there is a sulphide case formed at the surface of part, the constituents of the sulphide case are complicated, not a single sulphide such as ferrous sulphide or iron sulphide, and which has a detrimental influence on the coefficient of friction, and on the resistance to wear and to seizure. Furthermore, it is difficult and complicated to control the proportion of the nitrogen content to the sulphur content in the case to a desirable and exact degree. Therefore, an uneven composition and unstable quality would be resulted from the conditions mentioned above. The Huanan Polytechnical College has developed a sulphurizing process with a single gas instead of the said nitrosulphurizing in which a sulphide is used as medium and special-purpose sulphurizing furnace is used to hold temperature at 160°C and more, and thereby a case containing ferrous sulphide - (FeS) and iron disulphide ($FeS_2$) form at the surface of part (see "Heat Treatment of Metals" Vol.5, 1983). But there are some disadvantages relating to the process in that the medium is a sulphide, therefore besides sulphure, the sulphurizing atmosphere contains some other components, which has a detrimental influence on the quality of the case, much more some sulphides are poisonous, such as $H_2S$. Furthermore, there are not only ferrous sulphide but also iron disulphide formed with the said process in which the former is favourable and the latter is harmful to the resistance to wear. Besides these, the treating temperature used in the said process is rather high.

In recent years, a sulphurizing process by means of direct gasifying the solid sulphur was developed (see "Textil Transactions" Vol.2, "1983;" Hubei Machinery" Vol.4, 1981). With this process, the solid sulphur is heated to be gasified, then the sulphur-containing gas will be ionized under the action of electric field, thereby the surface of part being sulphurized. There is a comparatively satis-factory effect resulted from that the solid sulphur is used as the sulphurizing medium and thereby the said disadvantages resulted from sulphide are overcome. But there are still some shortcomings. Firstly, the process is a lightless discharge, namely, the sulphur-containing gas is ionized under a low-voltage field condition (300-500 V). Secondly, the solid sulphur which is loaded in a steel box is also located on the cathode table along with the parts being treated and thereby it is difficult to control the sulphur-gasifying temperature and the gasifying quantity. Thirdly, the part and the solid sulphur are heated by an inert gas discharge, therefore, the inert gas would be pumped out from the vacuum furnace after the temperature is raised to the desirable level in order to leave the sulphur-containing gas in the furnace and thus the operation is complicated and expensive.

The process of the present invention is an improved and developed version of the solid suphur-gasifying and sulphurizing process mentioned above. One of the objects of the present invention is to provide a sulphurizing process by means of direct heating the solid sulphur and gasifying it, which process overcomes the shortcomings mentioned above resulted from the said processes, and to attain a better sulphurizing quality than that resulted from other processes, an even and single constituent existed in the sulphurized case and thick case. The other object of the present invention is to provide an equipment to carry out the process of the present invention.

The keypoint of the gas sulphurizing is to produce a sulphur-containing gas. The advantages resulted from the present process in which the

sulphur-containing gas is made from the pure solid sulphur, not from sulphide, by direct heating are: the component of the gas is single, not like sulphide containing other components and thus it makes the controlling and the regulating simple; the component (ferrous sulphide) of the sulphurized case at the surface is also single and there is no influence and disturbance resulted from other elements. Sulphur is presented as a solid state under normal atmosphere and the boiling point of which is 441°C. But the boiling point would be lowered rapidly at low pressure, for example, the boiling point is 188.8°C at 1 Torr, and the boiling point would be less when the pressure decreases further. From this, the parts located on the cathode table of vacuum furnace will be sulphurized by means of heating and gasifying sulphur at low pressure (l-$10^{-2}$ Torr), applying a direct voltage field to ionize the gasified sulphure and bombarding the cathode with the high-speed positive sulphur ions, thus the parts located on cathode table is sulphurized. The process of present invention is chacterized by that the sulphur-containing gas is glow discharged under the action of high voltage (450-1500 V) field and the duration of glow discharge ganerally is 1-4 hours. Because of the glow discharging, the sulphurizing is speeded up and the sulphurized case depth is increased. Furthermore, because of the glow discharging, the parts may be heated only by means of electron bombarding. Generally, the temperature of parts is controlled between 140-300°C. Therefore, the temperature of the heated parts may be regulated through regulating the field voltage, but in the case of lightless discharging, the parts are heated only through inert gas. In addition, because of the glow discharging, the heating and gasifying of sulphure are flexible, for example, they may be carried out by means of a low voltage supply when sulphur is located on the cathode table just as the case of lightless discharging, or sulphur is located in the furnace other than the cathode table, or even outside the furnace. There is such an advantage in that the gas-sulphurizing operation may be carried out following the carburizing, nitriding or carbonitriding when the furnace temperature is lowered to the sulphurizing levie. Thus, the working hours and energy resource consumption may be extremely reduced.

Now, the invention will be described in detail with reference to the accompanving drawings and embodiments.

The best embodiment: Fig. 1 is a schematic diagram of the equipment according to present invention.

The part to be treated 5 is loaded on the cathode table 4 in the reacting chamber I of vacuum furnace. The part is a ball bearing made of Gr15. The temperature of part 5 is measured and controlled with a thermocouple 7 and a temperature meter 12. Solid sulphur is loaded in the vapourizer 6 and the temperature of vaporizer is measured and controlled with a thermocouple 8 and a temperature meter 10. The vaporizer 6 is heated with electric energy supplied from the low-voltage supply 11. The vaporizer shown in the figure is located in the reacting chamber 1, outside the cathode table 4, but it may be located on the cathode 4 or outside the reacting chamber 1 (furnace). The steps to sulphurize are as follows: firstly, the vacuum pump 16 is started, in the meantime, the reacting chamber 1 is pumped out; then the low voltage supply 11 is turned on when the pressure reaches about $10^{-2}$ Torr, and thus the temperature of vaporizer 6 starts to raise, because the pressure is lowered to $10^{-2}$ Torr, solid sulphur will be gasified when the vaporizer 6 is heated to more than 140°C (the gasifying temperature of solid sulphur ranges from 140°C to 200°C in this embodiment); when the gasified sulphur enters the reacting chamber 1, the pressure in the reacting chamber 1 is gradually raising, the temperature of vaporizer 6 is controlled by regulating the current supplied from the low-votage supply 11 and thereby the quantity of gas resulted from sulphur gasifying may be regulated and controlled; further, the pressure in the reacting chamber 1 may also be controlled; of course, the pressure in the reacting chamber 1 may also be controlled through regulating the relation between the vapourizing speed and the pumping speed (i.e. the vacuum pump still keeps running); when the pressure in the reacting chamber 1 is steadily in the desirable range (about 1 Torr for the present embodiment) through known precedures, the high voltage direct supply 3 (voltage ranges from 0 V to 1500 V) is turned on and the voltage of which is controlled between 450 V and 1500 V, then a high voltage field is formed among the cathode 4, part 5 and anode 2, then, by the action of the field, gaseous sulphur is ionized and the positive sulphur ions will bombard the cathode 4 and part 5 to form glow discharge and thereby to raise the temperature of the part; finally, because of the physical and chemical reactions existing between gaseous sulphur and the part, a case of sulphide is formed at the surface of the part, generally, the duration of glow discharge is controlled between 1 h and 4 hs, the part temperature is controlled between 140°C and 300°C. The temperature-controlling means is conventional.

Now the results of the sulphurized rolling bearing will be given below.

The sulphurized rolling bearing is a 204 single-row radial ball bearing. The bearing is subjected to a life test with a model 7501-type lever tester. The testing conditions are: 2400 r/min, radial load 190

kg, no lubricant agent. The bearing tested ran continually for 200 hrs without fatigue damage. As to the same kind of bearings not subjected to the sulphurizing process, the bearings (ball, outer races inner races and cages) all were burnt when they ran only for 80 minutes, the shortest one only for 35 minutes. The case depth of sulphurizing is 120 μm which is extremely greater than the case depth formed with other processes.

The other embodiments according to the present invention are described as follows:

(I) sliding bearings made of grey iron, spheroidized iron, 20C, 45C, 40Cr: After gas sulphurizing, the life of the bearings extended to 1-3 times under no oil or less oil condition.

(2) shafts such as straight shafts made of 45C, crankshafts made of steel or iron, reverting shafts (45C) for glassbottle-making machine: After sulphurizing and forming FeS, the wear was decreased to 70-20% of the usual case under lubrication condition and to 20% under less oil condition.

(3) pistons, piston rings and cylinder sleeves made of steel or iron for internal combustion engine, air compressor, hydraulic press: After sulphurizing, the life of the parts mentioned above may extend 25% and more.

(4) cutting tools such as high-speed steel tools and pinion shaped cutters: The fineness of the machined part is raised, if the sulphurized cutter is used for it. As to the sulphurized tap which is used for cutting the stainless parts, the life of which extended about 20%.

(5) traveller: The which was already subjected to carbonitriding is made of 20C. After sulphurizing, the life of which may extend 100%-200% and the life of the traveller may extend 60-100%.

(6) gears: As to the high precision gears and worms which have been subjected to sulphurizing, the seizure disappeared. From this, the bronze gears or worms which are used for preventing from seizure may be replaced with those made of steel or iron which have been subjected to sulphurizing. As to such gears which ran under poor lubrication condition, the life of which may raise 50%-200%.

(7) dies such as wire-drawing dies: Because the sulphurizing process may improve the lubricity of the surface of part, the quality of the worked part may be improved.

(8) parts of a sewing machine: After forming FeS at the surface of part, the life of which may raise 50% and more.

(9) guiding rail: After sulphurizing according to the present process, the quality of which may be improved.

(10) magnetic head: After gas sulphurizing, the life of which is raised without any failure in sound-reproducing effect.

The gas sulphurizing process and the equipment used in the embodiments mentioned above are the same used in the rolling bearing embodiment. Ferrous sulphide would be formed at the surface by means of the process and equipment and the case depth generally is 100-120 μm, at least 20 μm.

The equipment introduced in the embodiments mentioned above is the main body of the equipment. In order to make the equipment run normal, the equipment should be equipped with some devices such as vacuum gauge 9 for controlling pressure, flow meter I9 for controlling flow, some valves I3,I4,I8, waste gas filter I7, cold trap I5 for condensating reactant, gas bomb 20 and observing window 2I, which all are known for the skills in the art.

A detailed description has been made through the embodiments mentioned above but the present invention is not to be limited within the said embodiments. The present invention may be applied not only to the parts made of steel or iron for forming ferrous sulphide at the surface but also to the parts made of other metals for forming a sulphide case at the surface, for example, for forming NiS, $Nis_2$, at the surface of parts made of Ni or Ni alloy, for forming $MoS_2$ at the surface of parts made of Mo and Mo alloy, for forming CuS, $CuS_2$ at the surface of parts made of Cu and Cu alloy and for forming CoS at the surface of parts made of Co and Co alloy.

In summary, the advantages of the process and equipment presented by present invention are as follows:

I. With the process in which solid sulphur is heated directly, then gasified and thereby glow discharged in the high voltage field, the sulphurizing processing will speed up while an even and thick sulphurized case will be attained.

2. It is unnecessary to introduce inert gas for heating the parts because the parts would be heated by means of bombardment of sulphur ions to parts under glow discharge condition.

3. The vaporizer loaded with solid sulphur may be heated by low-voltage supply. From this, it is easy to control the heating temperature exactly for vaporizer and the vaporizer may be located on the cathode table or beside it.

4. The sulphide cases with different constituents and depths may be formed by means of regulating the pressure in the reacting chamber, the working-gas density, the temperature of part, the duration of forming sulphide and electric current or voltage between the cathode and anode.

5. The process of present invention has many uses and may be used not only for parts made of steel or iron, but also for parts made of other metals.

## Claims

1. A process used to form a sulphide case at the surface of metal part (5) by means of heating and gasifying sulphur comprises: loading the metal parts (5) on a cathode table (4) in a reacting chamber (1) of vacuum furnace and loading solid sulphur in the same chamber (1), under the vacuum conditions $1\text{-}10^{-2}$ Torr, heating sulphur up to the boiling point thereof and then sulphur comes on to be gasified, then the reacting chamber (1) is full of the gasified sulphur, in the meantime, an electric field is applied to the gasified sulphur between the cathode (4) and anode (2), and then the gasified sulphur starts to be ionized, the formed positive sulphur ions will bombard the metal parts - (5) on the cathode table (4) and a sulphide case will be formed at the surface of parts (5), the process is characterized by that the solid sulphur comes to be gasified by direct heating, the gasified sulphur is ionized and glow discharged under a high-voltage direct electric field, thereby the surface of metal part (5) is sulphurized under the glow discharge.

2. The process according to claim 1, characterized by that the voltage of direct field ranges from 450 V to 1500 V when glow discharge occurs.

3. The process according to claim 1, characterized by that the solid sulphur is heated with low voltage supply (11).

4. The process according to claim 1, characterized by that the temperature of teh heated part (5) is between 140 and 300°C.

5. The process according to claim 1 or 3, characterized by that the heating temperature to gasify the solid sulphur is between 140 and 200°C.

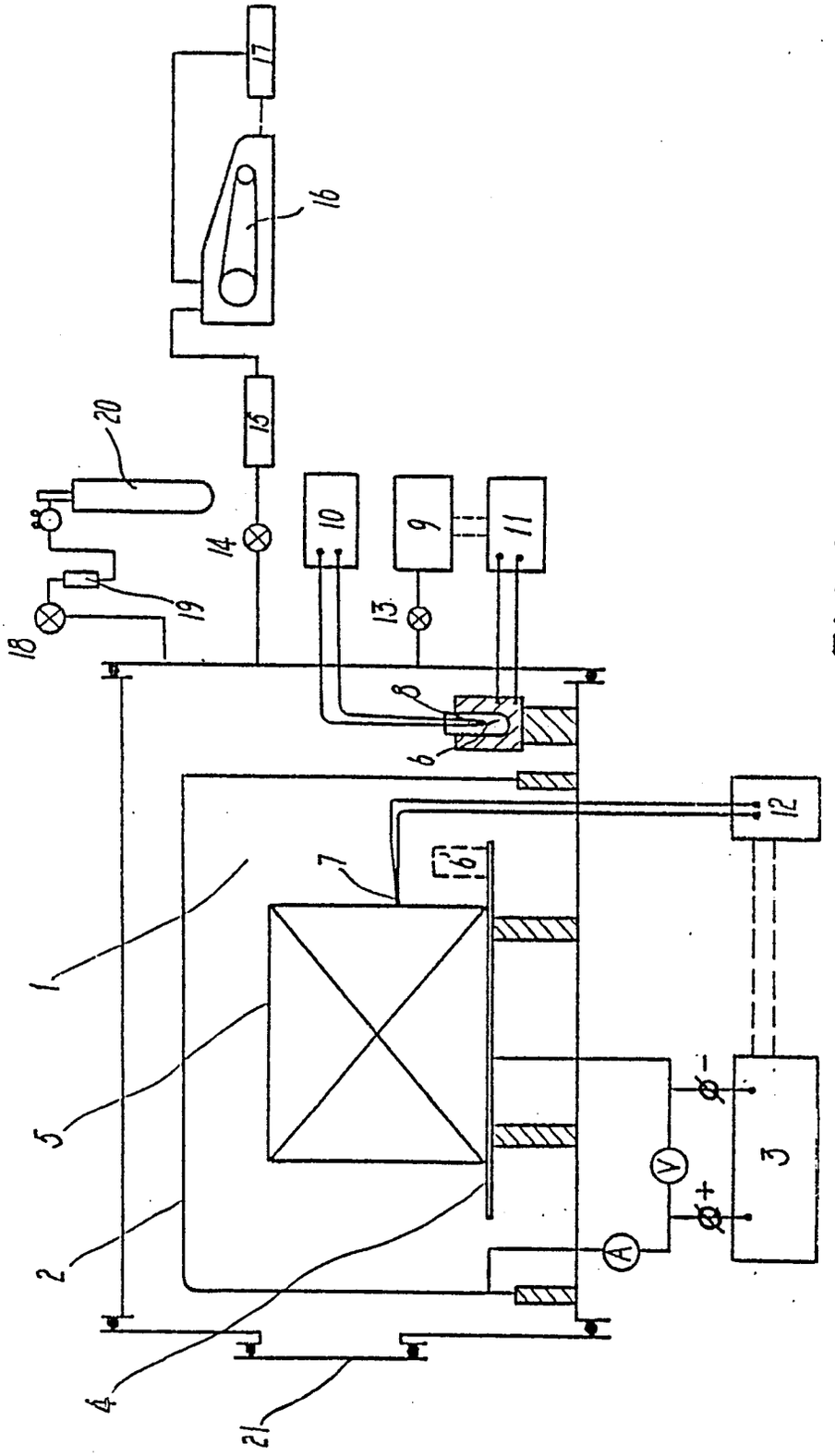
6. The process according to claim 1 or 3, characterized by that the solid sulphur is heated and gasified outside the cathode table (4).

7. The process according to claim 1 or 2, characterized by that the duration of glow discharge ranges from 1 hour to 4 hours.

8. An equipment to as sulphurize the metal parts (5) at the surface and thereby to form a sulphide case thereon, characterized by that it comprises: a vacuum reacting chamber (1), a cathode table (4) which is used to support the metal parts (5) and an anode (2) which are located in the vacuum reacting chamber (1) and a vapourizer (6) to hold the solid sulphur.

9. The equipment according to claim 8, characterized by that the vapourizer (6) is located on the cathode table (4).

10. The equipment according to claim 8, characterized by that the vapourizer (6) is located outside the cathode table (4).

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# EUROPEAN SEARCH REPORT

Application number

EP 86 11 2510

## 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.4) |
|---|---|---|---|
| A | GB-A-1 474 358 (K.K. DAINI SEIKOSHA) * Figures; page 1, lines 59-77; page 2, line 1; examples 1,3 * | 1,2,4, 6,8,10 | C 23 C 14/32 |
| A | EP-A-0 047 456 (WADA AYAO) * Figures 2,3; claims 1-18 * | 1,8 | |
| A | US-A-4 039 416 (G.W. WHITE) * Claims 1-4,7,8 * | 1,8 | |
| A | FR-A-1 273 518 (ASSOCIATED ELECTRICAL INDUSTRIES) * Figure 1; claims * | 1,3 | |
| A | GB-A-1 133 397 (HUGHES AIRCRAFT COMPANY) * Figures * | 1,3 | TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 23 C |
| A | US-A-3 472 679 (S.W. ING, Jr.) | | |
| A | PATENTS ABSTRACTS OF JAPAN, vol. 1, no. 120, 12th Oktober 1977, page 2834 C 77; & JP-A-52 82 683 (SUWA SEIKOSHA K.K.) 11-07-1977 | | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 19-01-1987 | ELSEN D.B.A. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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