(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 October 2005 (20.10.2005)

PCT

(10) International Publication Number
WO 2005/099048 A1

(51) International Patent Classification[7]: H01R 39/22, 43/12

(21) International Application Number: PCT/EP2004/004655

(22) International Filing Date: 8 April 2004 (08.04.2004)

(25) Filing Language: English

(26) Publication Language: English

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/099048 A1

(54) **Title:** LEAD-FREE BRUSH GRADE FOR HIGH TEMPERATURE APPLICATIONS

(57) **Abstract:** Sliding contact element for electric motors working with high current densities, such as gear reduced starters, comprising copper particles, black mix particles that result from milling a mixture of graphite particles and organic binders, containing also as lubricant additives one or more lead-replacing metals or compounds thereof, typically tin, zinc, bismuth, manganese, their oxides or their carbonates, characterized in that it also comprises a solid lubricant that has a decomposition temperature in air higher than 450°C, such as tungsten disulphide or boron nitride.

LEAD-FREE BRUSH GRADE FOR HIGH TEMPERATURE APPLICATIONS

Technical field

This invention relates to brushes for low voltage applications that are often subjected to very high temperatures due to the high current densities to which they are exposed. This is particularly the case for brushes used in starters and engine cooling fans of automobiles and battery-powered tools.

Background of the invention

Commonly, lead is used to reduce the effect of over-heating of electrical motors that work for a long time with high current densities. However, the increasing environmental need to eliminate lead from carbon brushes has imposed the replacement of lead with more environmentally-friendly materials.

For example, lead was replaced with tin or zinc, or alloys thereof (EP - B - 0 525 222 - DEUTSCHE CARBONE AG). More recently, patent application DE - A – 102 01 923 (DEUTSCHE CARBONE AG) discloses the replacement of lead with tin, zinc, bismuth, alloys or compounds thereof (such as oxides, carbonates, etc...) for brushes that are often subjected to high temperatures due to the high current densities to which they are exposed. Nevertheless there remain some applications where those replacements are not sufficient.

For example, brushes for a 1.4kW permanent magnet, gear reduced starter work for much longer than brushes for standard starters. Over their lifetime, they are thus subjected to very high temperatures (400°C - 500°C) for several minutes (typically 5 minutes) whereas standard starters work only few seconds at lower temperatures. Tests have been designed and carried out to select appropriate brushes that may work under such severe conditions. One of them, called "battery run down test," is basically an overload test where a starter motor cranks the engine for 5 minutes without interruption (or until the battery runs down). In this particular test, the starter motor is supplied with a high density current for 5 minutes opposed to the 2 seconds needed for a "standard crank cycle" test. The extremely long cycle time overheats the brush, the brush box and the commutator to the point where the brush does not perform properly afterwards. It is just one example among many different tests which load a starter motor for an extended period of time, or with a higher current density than under normal operation when starting an internal combustion engine.

The solution disclosed by patent application DE - A – 102 01 923, consisting of adding ZnO, $ZnCO_3$ and/or Zn, does not overcome the severe temperature problem which arises when the "battery run down test" is performed. Thus, the brushes of prior art with lead-replacing materials do not give satisfactory results with the "battery run down test" and the applicant has looked for new brush materials that give a longer life for low voltage electrical motors.

Summary of the invention

The first object of the invention is a sliding contact element for high current densities , typically higher than 15 A/cm^2, comprising copper particles, black mix particles that result from milling a mixture of graphite particles and organic binders, and containing as lubricant additives one or more lead-replacing metals or compounds thereof, which typically belong to the group consisting of Sn, Zn, Bi, Mn, their alloys, their oxides and their basic carbonates, characterised in that it also comprises a solid lubricant that has a decomposition temperature in air higher than 450°C, i.e. approximately the decomposition temperature of molybdenum disulphide.

Preferably, the lead-replacing lubricant additive is Sn, Zn, ZnO or, more preferably, zinc basic carbonate $ZnCO_3$. Optionally, the sliding contact element comprises also abrasive particles such as silica or silicon carbide particles.

The applicant started from temperature measurements made during the "battery run down test." They showed that the temperature of lead-containing brushes exceeded 450°C but the temperature of brushes with $ZnCO_3$ reached over 500°C. Considering that the lubricating effect of graphite is greatly reduced at these temperatures, the applicant started with the idea that the brush should also contain at least one solid lubricant other than graphite and that such a solid lubricant should be stable at high temperatures such as 500°C or more.

Molybdenum disulphide (MoS_2) was usually used as an additional solid lubricant in lead-containing brushes. In the absence of lead, the temperature may rise above 500°C and the use of MoS_2 becomes unsatisfactory. Moreover, patent application JP- A - 53147 609 teaches the use of a sintered copper alloy for a brush material, said alloy containing a mix of tin, zinc and zinc sulphide. However JP- A - 53147 609 advises against the addition of molybdenum, tungsten or iron sulphides in such a copper alloy, because said sulphides decompose at the sintering temperature of the copper alloy.

In the present case, the applicant has not tried to manufacture a carbon-filled sintered copper alloy but has developed a manufacturing process of a brush material comprising a copper-filled carbon matrix. This material was obtained by heat treating a mix of copper particles, black mix particles (particles that result from milling a mix of graphite particles and organic binders), lead-replacing lubricant material particles and, optionally, abrasive particles. The mix was treated at a temperature below the usual sintering temperature of copper materials, typically at 720°C, in order to carbonize the organic binders or resins properly.

Taking into consideration the fact that tungsten disulphide and boron nitride have decomposition temperatures (in air) about 100°C and 500°C above that of MoS_2 respectively, the applicant supposed that they would be able on the one hand to remain substantially stable during the heat treatment of the brush material (if heated in an inert gas) and on the other hand to survive the "battery run down" test without losing their lubricating properties. The decomposition temperature of MoS_2 is approximately 450°C: if heated in the open air at such a temperature, the molybdenum disulphide oxidizes and decomposes, the oxidation reaction giving molybdenum and sulphur oxides. By adding in the brush material a solid lubricant such as tungsten disulphide or boron nitride instead of molybdenum disulphide, the applicant succeeded in obtaining brushes that were able to perform the battery run down test.

According to the invention, the sliding contact element for high current densities, typically higher than 15 A/cm^2, contains copper particles, black mix particles, particles of lead-replacing metals or compounds thereof, such as Zn, Sn, Bi or their oxides or their carbonates, and particles of solid lubricant such as tungsten disulphide or boron nitride, the weight content of copper being preferably between 30 and 70 %, the weight content of lead-replacing metals or compounds thereof being preferably between 0.5 and 5 %, and the weight content of solid lubricant that has a decomposition temperature higher than 450°C being preferably between 0.5 % and 8%.

Another object of the present invention is a process for manufacturing a sliding contact element for high current densities, typically higher than 15 A/cm^2, containing as lubricant additives one or more lead-replacing metals or compounds thereof (typically Sn, Zn, Bi, Mn or their alloys or their oxides or their basic carbonates) comprising the following steps:

a) mixing graphite, organic binders, such as phenolic resin, polyamid resin or pitch;

b) optionally drying the premix resulting from step a), preferably by applying heat below the lowest curing temperature of the organic binders;

c) milling and sizing said premix;

d) blending said premix with any combination of atomized copper, copper flakes and electrolytic copper powder;

e) compressing the resulting mixed powder;

f) sintering said compressed powder;

wherein abrasive additives, such as silica or silicon carbide particles, are optionally added either in premixing step a) or in blending step d);

wherein said lead-replacing metals or compounds are added either in premixing step a) or in blending step d);

characterized in that said solid lubricant having a decomposition temperature (in air) higher than 450°C is also introduced either in mixing step a) or in blending step d).

Preferably said lead-replacing metal or compound is zinc carbonate.

Preferably, said solid lubricant having a decomposition temperature in air higher than 450°C is either tungsten disulphide or boron nitride.

Sintering step f) is preferably carried out at approximately 720°C in an inert atmosphere, typically containing mostly hydrogen. At such a temperature level the organic binders or resins are properly carbonized. However, lower temperatures are also possible with longer sintering times.

The resulting sintered material is machined to the desired shape of the sliding contact element. If this sliding contact element is an electrical motor brush, the blend is compressed in a mould also containing the end of a shunt wire, then sintered and machined to the wanted shape.

Example

In this example, all the percentages are weight percentages.

Brushes for a gear reduced starter were manufactured by preparing a blend of 31% black mix particles, 65% copper powder and 4% tungsten disulphide WS2. The black mix particles were obtained by mixing, milling and sizing a premix comprising 82% graphite, 12% phenolic resin and 8% zinc carbonate. The blend powder was then compressed in a mould that also contained the end of a shunt wire and sintered at 720°C in a non-oxidizing atmosphere containing mostly hydrogen. At least, brushes were machined to obtain the desired shape.

40 of said brushes have been subjected to a battery run down test (BRD test) consisting of

a) applying continuously a current density of 100 A/cm2 for 300 seconds through the sliding contact surface between the brush and the motor collector and

b) lasting afterwards at least 10 000 cycles of regular start.

All of said 40 brushes performed satisfactorily this BRD test.

Alternative brushes were manufactured with a similar process, without adding tungsten disulphide: a blend containing 65% copper powder and 31% black mix particles (82% graphite, 12% phenolic resin, 8% ZnCO3) and 4% MoS_2 was compressed, sintered and machined. 40 of these brushes were subjected to the same battery run down test: they lasted only between several hundred (approximately 300) to a few thousand (approximately 4500) cycles of regular test afterwards. Thus, none of them was able to perform the BRD test: the plastic brush holders melted in such a manner that they were no more able to hold the brush against the commutator and the commutators showed severe damage.

CLAIMS

1. Sliding contact element for high current densities, typically higher than 15 A/cm2 comprising copper particles, black mix particles that result from milling a mixture of graphite particles and organic binders, and containing as lubricant additives one or more lead-replacing metals or compounds thereof, which typically belong to the group consisting of Sn, Zn, Bi, Mn, their alloys, their oxides and their basic carbonates, characterized in that it also comprises a solid lubricant that has a decomposition temperature in air higher than 450°C.

2. Sliding contact element according to claim 1 wherein said solid lubricant is tungsten disulphide.

3. Sliding contact element according to claim 1 wherein said solid lubricant is boron nitride.

4. Sliding contact element according to any one of claims 1 to 3, wherein the weight percentage of said copper particles is between 30% and 70%, the weight percentage of said lead-replacing metals or compounds thereof is between 0.5% and 5% and the weight percentage of said solid content is between 0.5% and 8%.

5. Process for manufacturing a sliding contact element for high current densities according to anyone of claims 1 to 4, containing as lubricant additives one or more lead-replacing metals or compounds thereof, which typically belong to the group consisting of Sn, Zn, Bi, Mn, their alloys, their oxides and their basic carbonates, comprising the following steps:
a) mixing graphite, organic binders;

b) optionally drying the premix resulting from step a), preferably by applying heat below the minimal curing temperature of the organic binders;

c) milling and sizing said premix;

d) blending said premix with any combination of atomized, flake and electrolytic copper powder;

e) compressing the resulting mixed particles;

f) sintering said compressed particles;

wherein abrasive additives, such as silica or silicon carbide, are optionally added either in premixing step a) or in blending step d),

wherein said lead-replacing metals or compounds are added either in premixing step a) or in blending step d),

characterized in that said solid lubricant having a decomposition temperature in air higher than 450°C is also introduced either in the mixing step a) or in the blending step d).

6. Process for manufacturing a sliding contact element according to claim 4, wherein said lead-replacing metal or compound is zinc basic carbonate ZnCO3.

7. Process for manufacturing a sliding contact element according to claim 4 or 5, wherein said solid lubricant having a decomposition temperature higher than 450°C is tungsten disulphide.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/004655

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01R39/22 H01R43/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
1 December 2004	10/12/2004

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/004655

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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