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2,985,532

ELECTRICAL CONTACTS

Johann Simon Streicher, Spring Valley, N.Y., assignor, by mesne assignments, to Engelhard Industries, Inc., a corporation of Delaware

No Drawing. Filed Dec. 5, 1957, Ser. No. 700,767

4 Claims. (Cl. 75—212)

The present invention relates to electrical contacts consisting substantially of powdered silver and, more specifically, to such contacts for heavy duty performance which are manufactured from powdered fine silver by the well known methods of shaping the fine silver powder with or without addition of other materials e.g. metal oxides, into pellets, sintering by heat treatment, followed either by coining into the desired shape and furnacing again or by hot and cold rolling.

Silver contacts obtained by this powder metal method were found to be superior to contacts of solid wrought silver. They show a higher electrical conductivity and less tendency to stick but, under the action of the arc during operation with heavy currents, especially of several hundred amperes, the powder grains sinter together thus forming larger grains and counteracting the advantages of the powder method. Therefore and in order to prevent sticking of those contacts it has been suggested to add metal oxides to the fine silver powder which, in some cases, during the process of sintering, are subject to fusion and are assumed to separate the silver grains from each other thereby inhibiting their growth during the subsequent working into contact elements and during performance. However, this method of incorporating intergranularly oxides which fuse below or at the sinter temperatures or oxides which do not fuse at the sinter temperatures or not even at the melting point of silver produced still unsatisfactory results due to the fact that by their mechanical incorporation into silver powder the complete stabilization of the smallest grain sizes cannot be obtained by this method, and furthermore, the addition of excessive amounts of oxides causes an increase of the millivolt drop across the electrically operating contacts and renders them brittle.

It has been found that by way of treating silver powder with a halogen or preferably with a solution of ammonium halide a chemical reaction takes place already at room temperature and a more enhanced reaction takes place at elevated temperatures; due to that reaction silver halide is forming in situ upon the reacting silver powder; silver halide is deposited in extremely fine spongy state and in such uniform distribution upon the fine silver carrier as it cannot be obtained by mechanical mixing or fusion.

Tests revealed now that by way of submitting silver powder to such a halide treatment, preferably to the ammonium chloride treatment, and by providing it with spongy silver chloride in definite amounts an efficient method is given to incorporate into fine silver powder a very efficient grain stabilizer: Said grain stabilizer can be, of course, in the first place either silver halide alone or, in the second place, silver halide in combination with any suitable oxide or oxide mixture. On heating such combinations, after pressing such powders into suitable contact pellets the suddenly fusing silver halide having, on fusion, the property of wetting the silver grain surfaces, flows rapidly into the intergranular space, or, in presence

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of oxide powder it also wets the oxide particles and carries them into the intergranular space of the silver powder, effecting alone or together with the oxide powder particles an extremely efficient grain stabilization of the fine silver; the distribution of the silver halide or of the silver halide in combination with oxide is of a uniformity as it can never be obtained by mechanical mixing and subsequent compacting of silver powder and oxide powder.

In accordance with the invention, powdered silver with or without addition of other substances as e.g. metal powder or oxides is treated with a halogen or a solution of one or more halides to cover each grain at least partly. The preferred agent is ammonium chloride, but equally good results are obtained with other halides. The metallic silver in shape of silver powder reacts with the ammonium halide solutions already at room temperatures, but slowly; it is made to react faster at higher temperatures, on the steam bath or by heating on hot plates or in a drying oven. A coating of one or more silver halides is formed on the surface of each grain. It may be assumed that each silver grain being in contact with halide actually reacts individually and forms a discontinuous coating of spongy silver halide which presumably consists of single particles dispersed upon its surface. As the reaction progresses the coating becomes more and more continuous, until no more free silver surface is presented to the halide solution. Of course the desired amount is substantially less than the quantity obtained by complete reaction of the silver, hence the halide content of the solution will be chosen according to the concentration of halide desired in the finished product. By reacting ammonium halide with silver powder ammonia and hydrogen are liberated and the end of the reaction is indicated by the cessation of gas production.

It has been established by tests that e.g. about 0.8% to 6% by weight of silver chloride in the finished powder gives the best results and about 1% seems to be the amount where sufficient coating of the silver grains is accomplished to prevent grain growth. An excess of silver halide causes exudations either during the process of hot extrusion when worked into contact elements or when the silver powders or the mixtures of silver powder and oxide powder are shaped into contact pellets by way of coining and subsequent furnacing.

As mentioned before the silver contacts for heavy currents loads are provided with a variety of metal oxides, with mixtures of metal oxides, especially with metal oxides melting above fine silver. Contacts of this type show less the tendency to stick than pure fine silver contacts; they were found to stick less as the oxide contents increase; however, as the oxide content increases a decrease in conductivity is effected and the millivolt drop across the operating contacts increases, thereby nullifying the usefulness of the oxides with regard to improving silver as contact material.

It was found that the conductivity of contacts made from fine silver powder in admixture with metal oxides can be improved, as well, by the use of silver powder coated with spongy silver halide whereby their non-sticking properties under heavy current loads are not only generally maintained but they are improved to an extent that their non-sticking properties come already into evidence with relatively small amounts of oxide; therefore, due to their relatively small oxide content they are able to operate supremely with a small millivolt drop.

The preferred method to incorporate the oxides into the mixture consists in coating the silver powder with silver halide to the desired extent, followed by mixing with the powdered metal oxide and compacting by pressing and sintering. However, similar results are obtained by mixing the oxide and silver powders first and treating

the mixture with halogen or with a solution containing ammonium halide whereby only the metallic silver reacts. Tests were made with oxides of chromium, manganese, iron, cobalt, nickel, wolfram, copper, molybdenum, uranium, rhodium, ruthenium, palladium, cadmium, and double and multiple combinations thereof as e.g. manganic-cupric oxide, nickelous oxide-cupric oxide, cadmium oxide-nickelous oxide, cadmium oxide-ferric oxide, cadmium oxide-cupric oxide, etc.

It was found that this invention works best with oxide powders which preceding their mixing with silver powder or with silver powder carrying the spongy silver halide have been changed from the usual amorphous state into the crystalline state, generally called the mineralized state and being comminuted after mineralization into subtle and superfine powder like mineral colors.

The following examples are given to illustrate the present invention.

Example 1.—100 g. of powdered fine silver, passing a 200 mesh sieve were mixed in the dry state with 2.68 g. of chemically pure ammonium chloride and 17 ml. of distilled water were added. The admixture was slowly heated in a Pyrex dish to about 200° to 250° C. until complete evaporation of the water was effected. After cooling the mixture, more distilled water was added, followed by heating, the procedure being repeated about 10–12 times until ammonia ceased to be expelled. Then the material was ground to a powder passing through a 170-mesh sieve.

The obtained powder contained about 10 per weight silver-chloride and was worked into contact elements by the known method of compacting into pellets at about 5 tons per square inch sintering in air at 550° C. for about 1 hour. When tested on a D.C.-single-break-contactor, at 300 amperes and 235 volts, operating with a static contact pressure of 450 g., during 300 operations only 3 sticks occurred. The average voltage drop across the contacts when passing 10 amperes was found to be 1.6 millivolts.

Example 2.—This example illustrates the addition of a metal oxide to the halided silver powder.

Mineralized copper oxide powder was ground to 200–300 mesh and 4.56 grams of this copper oxide were added to 101.07 grams of silver powder which had been treated with ammonium chloride to contain 1.07 grams of silver chloride. The mixture was homogenized by tumbling and then sieved through a 170 mesh screen. Discs were pressed at 5 tons per square inch, sintered at 780° C. in air for one hour, coined at 70 tons per square inch and refurnaced for one hour at 780° C. These discs were found to have a residual porosity of 3%, a hardness of Rockwell H56 and exhibited a millivolt drop of 3 to 4 millivolts. These contacts produced 12 light sticks when operated for 10,000 cycles at 300 amperes and 220 volts A.C.

Example 3.—This example deals with contacts obtained by hot and cold rolling.

11.4 grams of copper oxide powder were added to 1000 grams of fine silver containing 10.6 grams of silver chloride and homogenized by mixing. Slugs were pressed at 15 tons per square inch and sintered for 3 hours at 600° C. The slugs were hot rolled at 600 degrees C. from 6" x 1" x 1" in 24 passes to ½" square, being re-

heated after 3–4 passes to 600° C. The resulting rod was cold rolled with 20 to 30% area reductions and anneals at 400–600° C. and finally drawn to wire.

Contact rivets made from this material were operated for 4,000 cycles at 115 volts, 30 amperes with a closing pressure of 100 grams, a breaking pull of 75 grams and an opening speed of 1½" per second. No sticks were produced and the millivolt drop varied from 11–20, while fine silver rivets under the same conditions produced 114 sticks.

Example 4.—2.88 grams of chromium oxide were homogenized with 100 grams of fine silver covered by 1.06 grams of silver chloride, pressed and sintered as described in Example 2. The obtained pellets operated without sticks for 500 operations at 300 amperes and 235 volts. It was observed that the color of the pellets changed from green to reddish brown and they gained weight to the extent of 1.08% during sintering. Apparently silver chromate is formed.

Example 5.—20 grams of chromium oxide were mixed with 1000 grams of fine silver containing 10.70 grams of silver chloride and treated as described in Example 2.

Contact elements made from this material operated without sticks for 400 makes and breaks at 300 amperes and showed a millivolt drop of 2 to 3.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof and the invention includes all such modifications.

What is claimed is:

1. A method of manufacturing electrical contacts from powdered silver comprising adding to at least a portion of the silver powder an agent selected from the group consisting of a halogen and a solution containing ammonium halide, said agent being added in an amount sufficient to react with the silver and form in situ on the silver from 0.8 percent to 6.0 percent by weight of silver halide, thereafter compacting the powder into desired form and sintering the form to produce the electrical contact.

2. A method according to claim 1, in which the amount of formed silver halide is about 1% by weight.

3. A method according to claim 1, in which the silver powder is admixed with from about 1.0 percent to about 4.5 percent of an oxide selected from the group consisting of oxides of copper, chromium, tin, cadmium, iron, ruthenium, nickel, manganese and molybdenum after the formation of the silver halide.

4. A method according to claim 1, in which the silver powder is admixed with from about 1.0 percent to about 4.5 percent of an oxide selected from the group consisting of oxides of copper, chromium, tin, cadmium, iron, ruthenium, nickel, manganese and molybdenum prior to the addition of the agent.

References Cited in the file of this patent

UNITED STATES PATENTS

1,599,618	Koehler	Sept. 14, 1926
1,829,635	Davey	Oct. 27, 1931
2,145,690	Henzel	Jan. 31, 1939
2,425,052	Swinehart	Aug. 5, 1947
2,572,662	Richardson et al.	Oct. 23, 1951