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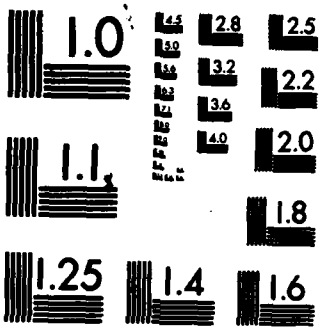

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by

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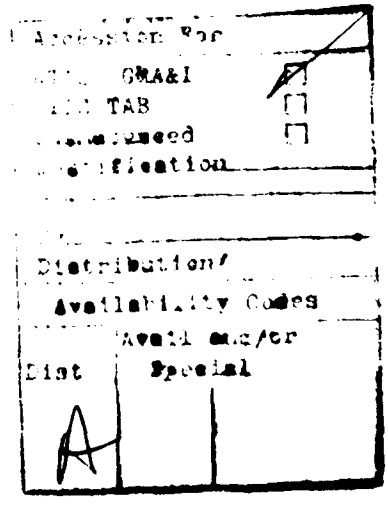

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FIBROUS CARBON-METALLIC MATERIALS AND A METHOD OF MANUFACTURING CARBON-METALLIC FIBROUS MATERIALS.

The object of the invention is a carbon substance covered with metal in the form of a composition containing various forms of fibrous materials, such as fabric, knitted fabric, unwoven fabric, yarn, cable, and metal, and a method of manufacturing the carbon-metallic fibrous materials by means of reduction without current of metal ions in an aqueous medium.

Known up to now are compositions containing only metallized carbon fibers in a free state. As an example, the patent description No. 1260189 from Great Britain gives a description of a reinforced carbon product containing carbon fibers associated with a carbon binder and an additive in the form of boron nitride, boron silicide and heat-resistant metal borides. On the other hand, Great Britain patent description No. 1302331 refers to metal parts reinforced by carbon fibers with a galvanized coating or as a result of a chemical

reaction in the gaseous phase of nickel in a layer 0.1-1μm. The carbon fibers covered with nickel are then covered by a fused metal, such as copper or aluminum. In patent description No. 1358869 of Great Britain there is a description of a carbon body combined with suitably applied and pressed carbon fibers, a carbonaceous binder and additives such as boron, niobium, silicon, tantalum and others.

United States patent description No. 3622283 concerns a composition of carbon fibers covered with a metallic medium based on tin, binding the fibers better in a parallel arrangement.

However, the novelty according to the invention consists of fibrous materials, fabrics, knitted fabrics, unwoven fabrics, yarn and cable in such a composition that they form a homogeneous substance with the metal. The known methods of producing carbon-metallic fibers are based on a galvanized coating on the fibers, as in Great Britain patent description No. 1375542, with copper, tin, lead or their alloys, or saturation with fused metals and their alloys as in patent description No. 3770488 from the United States of America, or on a distribution of introduced organometallic compounds as in Great Britain patent description No. 1255658 and patent description No. 3061465 from the United States of America.

The galvanized method of covering is not suited for products with a low degree of carbonization or with low electrical conductivity and therefore it is used only for continuous fibers with good conductivity along the axis.

The method based on saturation requires very complex vacuum-pressure apparatus working at the same time under conditions of high temperature (alloy or metal fusion) and high pressure.

On the other hand, the method assuming the introduction of organometallic compounds is limited to a few metals, such as Al and Zr, forming compounds subject to decomposition during carbonization.
The chemical methods applied anticipate a process of suitable activation treatment. The next methods of preparing the substrate for chemical metallization assume the use of a sensitizing treatment and activation with the use of expensive and short supply noble metals, e.g., palladium, gold and platinum, or compositions of them. We know from the article "Research on the effect of elevated temperatures on the properties of carbon fibers with metallic coating", presented in Fizika i chemija obrabotka materialow, No. 6/77, that the deposit of a metal from a salt solution onto fibers occurs only when the substrate acts as a catalyst in the formation of metal ions. In order to endow the surface of fibers with catalytic properties, they must be given a treatment based on oxidation with a 65% solution of HNO_3, sensitization ($SnCl_2$ 37g/l, HCl 40g/l, and activation ($PdCl_2$ 0.05g/l, HCl 10g/l).
In addition the carbon fibers can be modified -- with a dry gas treatment in which high temperatures are usually necessary -- Great Britain patent description No. 1343773 and Japanese patent description No. 24976. Usually active gases or neutral gases with the addition of an active gas are used for the gas treatment.
Another group of methods for treating the surface of carbon fibers is an electrochemical treatment, where the major process is electrolysis with the carbon fibers being used as the anode. According to patent description No. 3671411 of the United States of America and Great Britain patent description No. 1326736, fluorides, phosphates, NaOH, H_2SO_4 and others are used as electrolytic solutions.

According to the invention the carbon-metallic fibrous materials constitute a composition composed of fabric or knitted fabric or unwoven fabric or yarn, or cable and metal, where the thickness of the metallic layer is less than the diameter of the elementary fibers, and the metal content of the composition is no less than 3% by weight. The method of manufacturing the carbon-metallic fibrous materials by the chemical method according to the invention includes an initial activation treatment followed by a reduction of metal ions without current in an aqueous medium. Short-lived polarization is used as the initial activation treatment: anodic and cathodic polarization with a unidirectional or asymmetrical current. The most effective results are achieved with the use of current densities no greater than $100mA/cm^2$. As a result of anodic polarization the carbon product is initially hydrophobic, and thus not becoming wet by aqueous solutions, acquires hydrophilic features which makes good penetration of aqueous solutions deep into the product possible. Cathodic polarization forms active centers on the surface of the elementary fibers, making it possible to distribute metal in a medium containing reducing agents. The carbon-metallic fibrous materials, obtained in conformity with the invention, in comparison to the initial carbon fibrous materials, are distinguished by a 4-5 times greater strength and resistance to wear and by a temperature rise to about 400°C before the beginning of oxidation. The metallization process according to the invention is particularly anticipated for covering with metals which poorly wet carbon, such as Cu, Ni, Co, Cr and compositions of these metals. The method according to the invention can produce products with any degree of carbonization beginning at the thermal treatment of 600°C.

After metallization the product can constitute materials for direct application, depending on the kind of metal, such as electrical conductors, high temperature contacts, electrodes and plates in storage batteries and cells. In addition carbon-metallic fibrous materials can be semi-finished products for obtaining solid compositions.

Example 1. A carbon unwoven fabric obtained through carbonization of polyacrylic fabric is polarized anodically in a 1.5n solution of potassium carbonate, using a current load of 15mA/cm^2 for 30 seconds, and then is cathodically polarized in the same solution using a current of 25mA/cm^2 for a period of 60 seconds. The product is introduced into a metallizing bath containing 30g/1 of $CuCO_3 \cdot Cu(OH)_2$, 100g/1 of potassium-sodium tartrate, 50g/1 of KOH and 25g/1 of 40% formalin. The length of time in the metallizing bath amounts to 15 minutes at a process temperature of 28° C.

Example 2. A carbon fiber with a diagonal weave, obtained by carbonization of an oxidized fabric made of polyacrylic fibers, is subjected to anodic polarization in a solution of 0.2n of sulfuric acid with a current density of 35mA/cm^2 for 30 seconds, and then to cathodic polarization at a current density of 10mA/cm^2 for a period of 45 seconds in an aqueous solution containing 6g/1 of sodium hypophosphite. After contact with the metallizing solution for 10 minutes at a temperature of 85°C, we get a metallized product with a coating 5 micrometers thick on the elementary fibers.

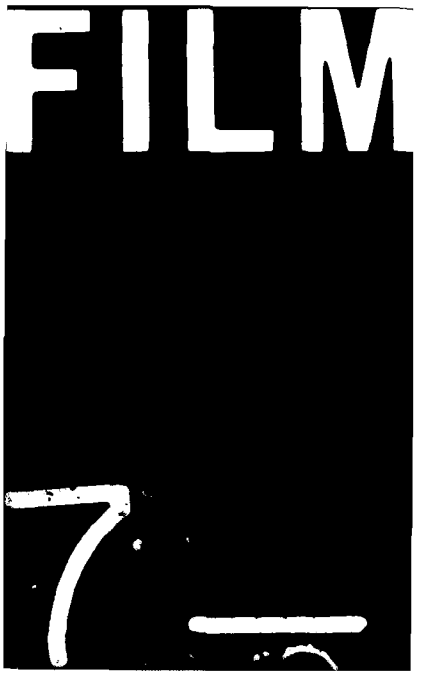
Patent Claims

1. Carbon-metallic fibrous materials characterized by the fact that they constitute a composition composed of a fabric, or a knitted fabric, or an unwoven fabric, or yarn, or cable and metal, where the thickness of the metallic coating is less than the diameter of the elementary

fibers and the metal content in the composition is no less than 3% by weight.

2. A method of manufacturing the carbon-metallic fibrous materials, including a preliminary activation treatment and reduction of metal ions without current in a aqueous medium, characterized by the fact that short-lived anodic and cathodic polarization is used as the initial activation treatment with a unidirectional or asymmetrical current.

3. Method according to claim 2, characterized by the fact that current densities no greater than 100mA/cm^2 are used.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