Formulating Precursors for Coating Metals and Ceramics

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A protocol has been devised for formulating low-vapor-pressure precursors for protective and conversion coatings on metallic and ceramic substrates. The ingredients of a precursor to which the protocol applies include additives with phosphate esters, or aryl phosphate esters in solution. Additives can include iron, chromium, and/or other transition metals. Alternative or additional additives can include magnesium compounds to facilitate growth of films on substrates that do not contain magnesium.

Formulation of a precursor begins with mixing of the ingredients into a high-vapor-pressure solvent to form a homogeneous solution. Then the solvent is extracted from the solution by evaporation — aided, if necessary, by vacuum and/or slight heating. The solvent is deemed to be completely extracted when the viscosity of the remaining solution closely resembles the viscosity of the phosphate ester or aryl phosphate ester. In addition, satisfactory removal of the solvent can be verified by means of a differential scanning calorimetry essay: the absence of endothermic processes for temperatures below 150 °C would indicate that the residual solvent has been eliminated from the solution beyond a detectable dilution level.

This work was done by Wilfredo Morales of **Glenn Research Center** *and Jorge E. Gatica and John T. Reye of Cleveland State University. Further information is contained in a TSP (see page 1)..*

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Commercial Technology Office, Attn: Steve Fedor, Mail Stop 4–8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17537-1.

Making Macroscopic Assemblies of Aligned Carbon Nanotubes

Nanotubes are aligned and manipulated with the help of magnetic and/or electric fields.

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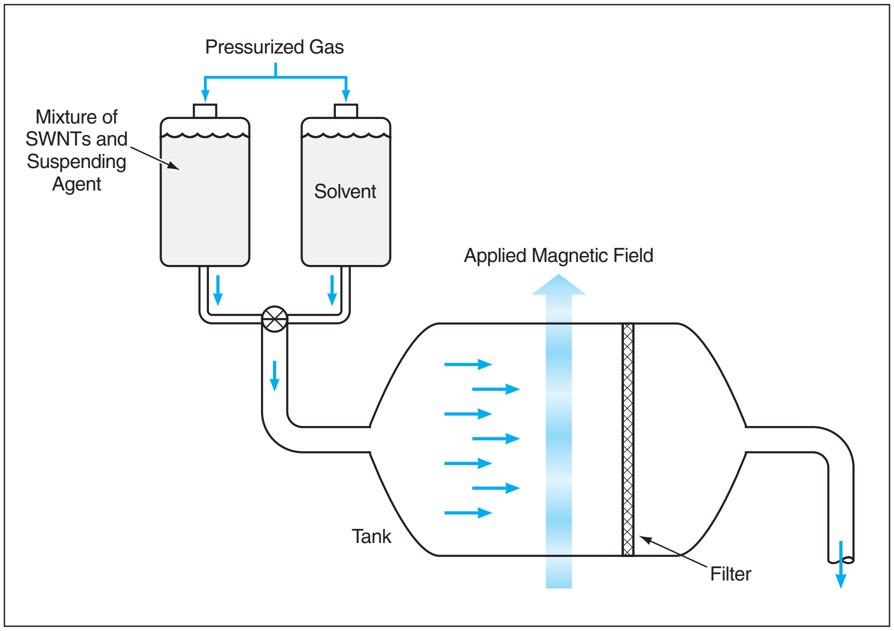
A method of aligning and assembling single-wall carbon nanotubes (SWNTs) to fabricate macroscopic structures has been invented. The method entails suspending SWNTs in a fluid, orienting the SWNTs by use of a magnetic and/or electric field, and then removing the aligned SWNTs from suspension in such a way as to assemble them while maintaining the alignment.

SWNTs are essentially tubular extensions of fullerene molecules. It is desirable to assemble aligned SWNTs into macroscopic structures because the common alignment of the SWNTs in such a structure makes it possible to exploit, on a macroscopic scale, the unique mechanical, chemical, and electrical properties that individual oriented SWNTs exhibit at the molecular level. Because of their small size and high electrical conductivity, carbon nanotubes, and especially SWNTs, are useful for making electrical connectors in integrated circuits. Carbon nanotubes can be used as antennas at optical frequencies, and as probes in scanning tunneling microscopes, atomic-force microscopes, and the like. Carbon nanotubes can be used with or instead of carbon black in tires. Carbon nanotubes are useful as supports for catalysts. Ropes of SWNTs are metallic and, as such, are potentially useful in some applications in which electrical conductors are needed — for example, they could be used as additives in formulating electrically conductive paints. Finally, macroscopic assemblies of aligned SWNTs can serve as templates for the growth of more and larger structures of the same type.

The great variety of tubular fullerene molecules and of the structures that



A **Solution Containing Suspended** SWNTs is made to flow through a magnetic field and a filter. The magnetic field orients the SWNTs predominantly parallel with each other in the plane of the filter. Hence, the SWNTs become deposited on the filter in alignment with each other.

could be formed by assembling them in various ways precludes a complete description of the present method within the limits of this article. It must suffice to present a typical example of the use of one of many possible variants of the method to form a membrane comprising SWNTs aligned substantially parallel to each other in the membrane plane. The apparatus used in this variant of the method (see figure) includes a reservoir containing SWNTs dispersed in a suspending agent (for example, dimethylformamide) and a reservoir containing a suitable solvent (for example, water mixed with a surfactant). By use of either pressurized gas supplied from upstream or suction from downstream, the suspension of SWNTs and the solvent are forced to mix and flow into a tank. A filter inside the tank contains pores small enough to prevent the passage of most SWNTs, but large enough to allow the passage of molecules of the solvent and suspending agent. The filter is oriented perpendicular to the flow path. A magnetic field parallel to the plane of the filter is applied.

The success of the method is based on the tendency of SWNTs to become aligned with their longitudinal axes parallel to an applied magnetic field. The alignment energy of an SWNT increases with the length of the SWNT and the magnetic-field strength. In order to obtain an acceptably small degree of statistical deviation of SWNTs of a given length from alignment with a magnetic field, one must make the field strong enough so that the thermal energy associated with rotation of an SWNT away from alignment is less than the alignment energy.

As the liquid passes through the filter, the aligned (more precisely, partially aligned) SWNTs become trapped on the filter. As SWNTs accumulate on the filter, they become attached to each other by van der Waals forces, thereby assembling themselves into a membrane. The flow of liquid and suspended SWNTs can be continued until the membrane has grown to the desired thickness, which would typically be of the order of 1 μm or more.

The membrane is removed from the screen, then subjected to a rinsing and drying process that removes the suspending agent and allows the SWNTs to come into more intimate contact, increasing the degree of van der Waals contact and thereby effectively strengthening bonds between adjacent aligned SWNTs. Further alignment and increase in the degree of van der Waals contact is achieved by annealing the membrane in an inert atmosphere at a temperature between 200 and 1,300 °C. Membranes consisting mostly of aligned SWNTs, with thicknesses >1 μm and areas >1 cm^2, have been produced by this method.

This work was done by Richard E. Smalley, Daniel T. Colbert, Ken A. Smith, Deron A. Walters, Michael J. Casavant, Xiaochuan Qin, Boris Yakobson, Robert H. Hauge, Rajesh Kumar Saini, Wan-Ting Chiung, and Charles B. Huffman of Rice University for **Johnson Space Center**.

In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:

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Refer to MSC-23302, volume and number of this NASA Tech Briefs *issue, and the page number.*