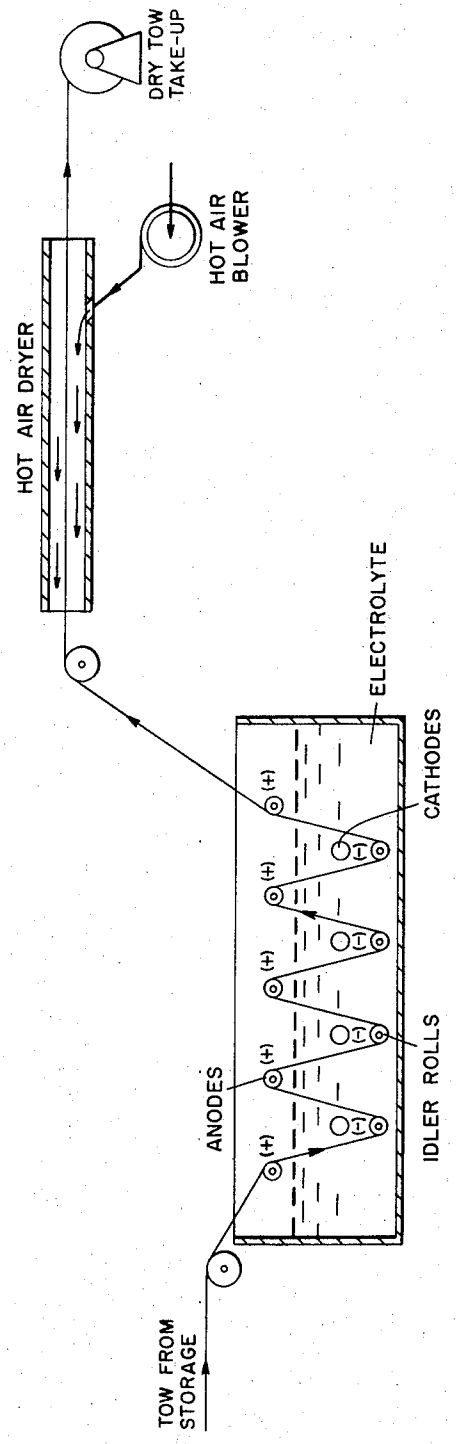
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PROCESS FOR ELECTROLYTIC TREATMENT OF GRAPHITE FIBERS

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PROCESS FOR ELECTROLYTIC TREATMENT OF GRAPHITE FIBERS

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ABSTRACT OF THE DISCLOSURE

This invention is an improved process for the electrolytic surface treatment of graphite fiber. In the process of of this invention organic or inorganic ammonium compounds which are water-soluble and which decompose to gaseous products below about 250° C. are employed. Residual material present in the fiber surface following electrolytic treatment is easily removed by heating of the fiber to volatilize residual material.

This invention relates to the electrolytic surface treatment of graphite fibers in which the electrolyte is an organic or inorganic ammonium compound which is soluble in water and which can be decomposed into volatile products by heating at a temperature below about 250° C.

Composite materials such as graphite fiber reinforced plastics are presently being manufactured as engineering materials and have found extensive use in areas of aircraft structural elements, underwater equipment, boat hulls and the like. Composite materials provide many combinations of properties not otherwise obtainable with previously known construction materials. However, the strength properties and permanence of the strength properties of composite materials, particularly in an adverse environment, is highly dependent on the interfacial bonding of the composites, i.e., the strength of the bonding between the graphite fiber and the composite resin matrix. Interlaminar shear strength value which is a measure of the degree of bonding or adhesiveness of a reinforcement to a resin matrix has been low for graphite fiber reinforced composites, therefore limiting the potential use of these materials.

Numerous processes have been developed to improve the adhesive characteristics of graphite fiber to a resin matrix to improve the interlaminar shear strength of the resulting composite material. One of the principal methods previously employed has been the electrolytic surface treatment of the fiber. In such processes the graphite fiber is subject to electrolytic reaction in an aqueous electrolyte whereby negative ions are attracted to the surface of the fiber acting as an anode, thereby modifying the fiber surface. As a result of this surface modification, subsequent bonding of the treated graphite fibers to resins is improved to such an extent that the shear strengths are increased many times with little or no loss in tensile strength.

The prior art recognizes numerous electrolytes generally employed in the form of aqueous solutions which can be used in the surface treatment of graphite fibers. Some of the electrolytes disclosed in the art for this purpose include sodium hydroxide, potassium hydroxide, phosphoric acid, nitric acid, sulfuric acid, and the like. One of the preferred electrolytes is aqueous sodium hydroxide. This material has been considered desirable since it has the advantage of having a high electrical conductivity which permits large numbers of fiber ends to be treated at high speed and low voltage in electrolytic baths. The principal disadvantage of the use of aqueous sodium hydroxide as an electrolyte is the difficulty of removing all of the sodium hydroxide electrolyte from the fiber. Removal of the electrolyte is achieved by rinsing the treated fiber with relatively pure water. Wash water must be pure since water

contaminants and residues left on the fiber surface from the electrolyte, such as $NaHCO_3$ or Na_2CO_3 cause voids in composites made from the fiber, oftentimes evidenced by surface blistering. Such voids or blisters are especially evident after boiling or exposing the composites to conditions of high humidity. In order to avoid the disadvantages inherent with the use of electrolytes such as sodium hydroxide, vigorous washing conditions with pure water must be employed to removed substantially all of the electrolyte residues. The vigorous washing of graphite fiber often results in entanglement of filaments and produces nets of loose filament which are difficult to remove, causing quality control problems in manufacture of the graphite fiber reinforced composites.

In accordance with this invention an electrolytic process for surface treating graphite fiber electrolytically is provided in which the improvement resides in use of organic and inorganic ammonium compounds dissolved in water which compounds will decompose substantially completely to gaseous products on heating at temperatures below about 250° C.

Illustrative organic and inorganic ammonium compounds which are soluble in water and which decompose to gaseous products on heating to temperatures below about 250° C. include ammonium hydroxide (NH_4OH), ammonium carbonate [$(NH_4)_2CO_3$], ammonium bicarbonate [$(NH_4)HCO_3$], ammonium carbamate

[$NH_4NH_2CO_2$],

ammonium benzoate [$NH_4 \cdot C_7H_5O_2$], ammonium dithionate [$(NH_4)_2S_2O_6$], ammonium hydrosulfide [NH_4HS], ammonium sulfite [$(NH_4)_2SO_3 \cdot H_2O$], ammonium thiosulfate [$(NH_4)_2S_2O_3$], ammonium tartrate [$(NH_4)_2C_4H_4O_6$], mixtures thereof and the like.

The electrolytic process of this invention to be effective must be conducted at potentials sufficient to liberate oxygen at the surface of the graphite fibers (anodes). Fiber electrical treatment levels are normalized to account for differing combinations of amperage level, throughput speed, and number of tows being treated by expressing the fiber treatment level as the coulombs of charge passed per inch of fiber length, i.e., as the ratio of total amperage per end to the throughput speed (in inches per second).

$$\frac{\text{coulombs}}{\text{inch}} = \frac{\text{amps}}{\text{inch/second}} = \frac{\text{coulombs/sec.}}{\text{inch/second}}$$

This definition of treatment level assumes that the degree of fiber treatment depends only on the amount of current passed through a unit length of fiber during treatment. This assumption is consistent with the general trends in the results of NOL short beam shear strength measurements obtained on epoxy resin composites made with fibers of varying degrees of treatment. In accordance with the process of this invention, fiber electrical treatment levels of from about 0.5 to 15 coulombs/inch can be employed. The preferred electrical treatment level is from about 2.0 to about 6.0 coulombs/inch.

The term "graphite fiber," as used herein, is intended to include both graphite fiber and carbon fiber prepared by heating polymeric fibrous materials such as polyacrylonitrile, polyvinyl alcohol, pitch, natural and regenerated cellulose and the like, to carbonizing or graphitizing temperatures.

The following examples will illustrate the process of this invention. In the examples, parts and percentages are by weight unless otherwise specified.

EXAMPLES 1–30

Graphite fibers are electrolytically treated employing the improved electrolytes of this invention as follows. Graphite fibers are pulled from an idler spool over a series of anodes and nonconductive idler rolls which are

mounted on stainless steel shafts, as illustrated in the drawing. The idler rolls are spaced apart intermittent the anodes and are submerged in the aqueous electrolyte. A series of graphite cathodes spaced apart, are also submerged in the electrolyte. A direct current power supply is used to apply the necessary potential across the anode and the cathode. The anodic side of the power supply is maintained at ground potential to reduce electrical hazards and to establish a reference point. The graphite fiber assumes negative potential in contact wtih the anodes and then functions as the anode in the electrolytic bath. The fiber electrical treatment level is set forth in Table I. The surface treated graphite fiber emerging from the outlet of the electrolytic cell is passed into a hot air dryer operating at a temperature ranging from about 93° C. at the inlet to 125° C. at the point of entry of the hot air to the dryer as is illustrated in the drawing. Residence time for the fiber within the dryer is about 5 minutes.

ceedings of 21st Annual Technical Conference SPI Reinforced Plastics Division, Section 8–D, February 1966.

Composite samples prepared as described are tested for short beam shear strength in accordance with ASTM–2344, (1) without further treatment and (2) after samples are boiled in water for seventy-two hours. The boiling test is an accelerated test to determine if blisters or voids will appear in composites made from treated graphite fiber. Results of this testing show no visual blistering of composites prepared from the graphite fiber treated in accordance with this invention which were subjected to the water boiling test. These results indicate substantially complete removal of the ammonium electrolyte and residual compounds from the electrolytically treated fiber as a result of the volatilization of both the electrolyte and the residual decomposition products during the drying operation performed after electrolysis. Shear strength retention is high.

TABLE I

Ex. No.	Electrolyte	Treatment level (coulombs/inch)	Average short beam shear strength (p.s.i.)	Average shear strength after 72 hrs. H_2O boil (p.s.i.)	Percent retention	Fiber type	Composite blistering after 72 hrs. H_2O boil
1	2.65 NNH_4OH	10	12,720 (Cv=2.2%)	11,560	90.9	Type HT	No.
2	2.65 NNH_4OH	10	12,770 (Cv=2.6%)	11,700	91.5	do	No.
3	2.65 NNH_4OH	2.5	12,590 (Cv=1.7%)			do	No.
4	2.65 NNH_4OH	5.0	13,030 (Cv=1.9%)			do	No.
5	2.65 NNH_4OH	5.0	5,400 (Cv=2.9%)			do	No.
6	2.65 NNH_4OH	3.0	4,470 (Cv=2.7%)			do	No.
7	2.65 NNH_4OH	3.0	11,770 (Cv=4.2%)	10,080	85.6	do	No.
8	2.65 NNH_4OH	3.0	6,090, 4,470 (Cv=4.4%)			do	No.
9	2.65 NNH_4OH	3.0	11,990 (Cv=1.0%)	10,760	89.7	do	No.
10	2.65 NNH_4OH	3.0	11,900 (Cv=2.2%)	10,940	91.9	do	No.
11	2.65 NNH_4OH	3.0	12,220 (Cv=2.5%)	10,580	86.6	do	No.
12	2.65 NNH_4OH	1.44	10,140 (Cv=8.0%)	9,210	90.8	do	No.
13	2.65 NNH_4OH	2.5	11,990 (Cv=6.5%)	10,740	89.6	do	No.
14	2.65 NNH_4OH	2.5	12,230 (Cv=3.4%)	11,110	90.8	do	No.
15	2.65 NNH_4OH	2.5	11,970 (Cv=6.9%)	11,240	93.9	do	No.
16	2.65 NNH_4OH	2.5	11,250 (Cv=8.0%)	10,570	93.9	do	No.
17	2.65 NNH_4OH	2.5	11,290 (Cv=6.7%)	10,650	94.3	do	No.
18	2.65 NNH_4OH	16	11,790			do	No.
19	2.65 NNH_4OH	10.8	12,800			do	No.
20	2.65 NNH_4OH	4.5	12,600			do	No.
21	2.65 NNH_4OH	4.5	12,200			do	No.
22	2.65 NNH_4OH	2.7	12,700			do	No.
23	2.65 NNH_4OH	2.7	11,900			do	No.
24	0.42 $N(NH_4)_2CO_3$	5.0	12,490	8,710	69.7	do	No.
25	0.42 $N(NH_4)_2CO_3$	10	11,980	9,690	80.9	do	No.
26	0.24 NNH_4HCO_3	5.0	10,620	9,285	87.4	Type A fiber	No.
27	0.5 NNH_4HCO_3	5.0	10,160	9,610	94.6	Type HT fiber	No.
28	0.24 NNH_4HCO_3	10	12,940	11,710	90.5	do	No.
29	0.24 NNH_4HCO_3	5	7,530	7,270	96.5	do	No.
30	0.24 NNH_4HCO_3	2.5	4,320	4,440	103	do	No.

NOTE.—Cv=Coefficient of variation, HT Fiber=Graphite fiber prepared from polyacrylonitrile precursor fiber—available commercially from Hercules Incorporated; A Fiber=Graphite fiber prepared from polyacrylonitrile precursor fiber—available commercially from Hercules Incorporated.

The dried treated graphite fiber is collected on a take-up roll at constant tension for subsequent use and testing. Graphite fiber surface treated as described and employing different electrolytes at various concentrations and different electrical levels as set forth in Table I are used to prepare composites employing ERLA 2256 resin (manufactured and available commercially from Union Carbide Corporation). The composite specimens are made in the form of an NOL ring containing about 60% by volume of treated graphite fiber. In preparation of the composite the graphite fiber is passed through the epoxy resin system, through a tensioning device, and onto a rotating mold. The whole system is enclosed in a vacuum chamber to provide a low void composite specimen. The mold is removed from the NOL winding device and placed in a curing oven to harden the resin. For the resin system described, the resin is cured for 2 hours at 125° C. followed by four hours at 155° C. The epoxy resin system employed is comprised of ERLA 2256 which is a mixture of 35% by weight of bis-2,3 epoxy cyclopentyl ether and 65% by weight of the diglycidyl ether of bisphenol A. The curing agent or hardener employed in this resin system is a eutectic mixture of metaphenylene diamine and methylene dianiline. A discussion of NOL ring specimens and their manufacture may be found in *Plastics Technology*, November 1958, pp. 1017–1024, and Pro-

It is noted that in Examples 5, 6 and 8 the composites exhibited poor shear strength. While the precise cause of this failure is not shown, it is believed to be due to inadequate control of electrical treatment level in the graphite fiber tow.

To further evaluate the surface treated fibers employing electrolytes of this invention, the treated fibers are dried and then refluxed in distilled water employing 20 parts of distilled water per one part of treated fiber. Following this refluxing the extract conductivity of the water is measured. Results reported in Table II indicate that the electrical conductivity of treated fiber without water washing is low. The fiber of Examples 1–5 is hot air dried as shown in the drawing. The fiber from Examples 6–30 are drum dried on a steam heated rotary drum having a surface temperature of about 120° C. Fiber contact time with the heated surface is from about 30 to about 90 seconds depending on throughout speed used. The high extract conductivity of the water in Example 12 is believed to be the result of residues left on the drum surface from improper prior washing of the drum. The conductivity values reported in Table II are similar in magnitude to those of graphite fiber subjected to electrolysis in which sodium hydroxide was the electrolyte and in which the fibers were thoroughly and repeatedly washed with pure water.

TABLE II

Electrolyte		Post treatment H_2O wash	H_2O Extract conductivity** (μmho/cm.)
Example number:			
1	2.65 NNH_4OH	None	29.6
2	2.65 NNH_4OH	Yes*	31.0
3	2.65 NNH_4OH	None	22.0
4	2.65 NNH_4OH	do	19.0
5	2.65 NNH_4OH	do	16.0
6	2.65 NNH_4OH	do	14.0
7	2.65 NNH_4OH	do	22.0
8	2.65 NNH_4OH	do	18.0
9	2.65 NNH_4OH	do	17.0
10	2.65 NNH_4OH	do	37.0
12	2.65 NNH_4OH	do	60.0
13	2.65 NNH_4OH	do	25.0
14	2.65 NNH_4OH	do	27.0
15	2.65 NNH_4OH	do	27.0
17	2.65 NNH_4OH	do	23.0
28	0.24 NNH_4HCO_3	do	50.0
29	0.24 NNH_4HCO_3	do	22.0
30	2.24 NNH_4HCO_3	do	9.0
Control	(1)		~2.0

[1] Boiled distilled water.
*Five (5) minute wash in counter current flow of tap H_2O.
**Electrical conductivity of H_2O extract measured at 25+° C. following British Standard 3266: 1969.

The following examples are control examples illustrating the use of sodium hydroxide as electrolyte.

EXAMPLES 31–40

The process of electrolytically surface treating graphite fiber as set forth in the description of Examples 1–30 is repeated employing 10% sodium hydroxide as the electrolyte. The electrical treatment level for these examples varies from about 2.0 to about 6.0 coulombs per inch. The surface treated graphite fiber emerging from the outlet of the electrolytic cell is washed with water to remove residual material including sodium hydroxide from the surface of the fiber. Washing is repeated until the water extract has a conductivity level of less than about 50 μmho/cm. Water extract conductivity is measured in all examples following British Standard 3266: 1969 entitled "Methods for the Determination of Conductivity, pH, Water Soluble Matter, Chloride and Sulfate in Aqueous Extracts of Textile Materials."

The washed graphite fibers are then used to make composite specimens following the procedure as set forth in Examples 1–30.

Examples 35, 77 and 39 are repeated in Examples 36, 38 and 40 respectively, with the exception that the fibers employed in Examples 36, 38 and 40 were subjected to additional water washings in an attempt to remove all traces of sodium hydroxide and residual products from the surface of the fiber following electrolysis. The composites prepared are tested following the procedures employed in Examples 1–30. Test results are set forth in Table III. It is clear from the data of Table III that even with numerous water washings of electrolytically surface treated graphite fibers in which sodium hydroxide is the electrolyte, that the incidence of blistering of the resultant composite subjected to a 72 hour water boil test is high.

In the process of this invention there are numerous factors which must be evaluated to determine preferred treatment conditions when employing the improved electrolytes of this invention. Thus, for example, it is known that the electrical resistances of graphite fibers prepared from different precursor materials and which have undergone prior treatments and prepared by varying methods will vary substantially. Also, the electrical resistance of various electrolytes suitable for use in the process of this invention will vary widely. Electrolytes such as ammonium carbonate and ammonium bicarbonate for example, are preferred over ammonium hydroxide from the standpoint of consumption of electricity in operation of the process of this invention since apparent bath resistance levels for ammonium hydroxide are about 12.5 times greater than the bath resistances of equal concentrations of ammonium carbonate and bicarbonate. Other factors which must be evaluated in an electrolytic process are residence time in the cell at a given electrolyte concentration and working voltage. These factors can be evaluated for each fiber type and cell system to achieve optimum performance of electrolytic suface treatment employing the improved electrolytes of this invention.

What I claim and desire to protect by Letters Patent is:

1. In the process of surface treating graphite fibers by electrolysis in an electrolytic bath in which the graphite fibers are in direct contact with and form a part of the anodes, and in which the electrical treatment level is sufficient to liberate oxygen at the surface of the graphite fibers, the improvement comprising employing as the electrolyte in aqueous solution, an organic or inorganic ammonium compound which substantially decomposes on heating at temperatures below about 250° C. to gaseous products.

2. The process of claim 1 in which the electrical treatment level is from about 0.5 to 15 coulombs of electrical charge per inch of graphite fiber.

3. The improved process of claim 1 in which the electrolyte is an organic or inorganic compound selected from the group consisting of ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, ammonium carbamate, ammonium benzoate, ammonium dithionate, ammonium hydrosulfite, ammonium sulfite, ammonium thiosulfate, ammonium tartrate, and mixtures thereof; and in which the electrical treatment level is from about 0.5 to about 15 coulombs of electrical charge per inch of graphite fiber.

4. The process of claim 3 in which the electrolyte is ammonium hydroxide.

5. The process of claim 3 in which the electrolyte is ammonium carbonate.

6. The process of claim 3 in which the electrolyte is ammonium bicarbonate.

7. The process of claim 3 in which the electrolyte is ammonium carbamate.

8. The process of claim 3 in which the electrolyte is ammonium benzoate.

9. The process of claim 3 in which the electrolyte is ammonium dithionate.

TABLE III

Electrolyte		Average short beam shear strength (p.s.i.)	Average shear strength after 72 hr. H_2O boil (p.s.i.)	Percent retention	Fiber type	Composite blistering after boil
Example number:						
31	10% NaOH	13,260	11,240	84.8	A	No.
32	10% NaOH	12,910	9,620	74.5	A	Yes.
33	10% NaOH	12,770	11,210	87.7	A	No.
34	10% NaOH	13,290	11,660	88	HT	No.
35	10% NaOH	12,930	10,650	82	HT	Yes.
36	10% NaOH	14,000	11,110	79	HT	Yes.
37	10% NaOH	13,310	9,830	74	HT	Yes.
38	10% NaOH	13,540	12,100	89	HT	Very little.
39	10% NaOH	13,100	11,040	84	HT	Yes.
40	10% NaOH	13,130	12,360	94	HT	No.

10. The process of claim 3 in which the electrolyte is ammonium hydrosulfite.

11. The process of claim 3 in which the electrolyte is ammonium sulfite.

12. The process of claim 3 in which the electrolyte is ammonium thiosulfate.

13. The process of claim 3 in which the electrolyte is ammonium tartrate.

References Cited

UNITED STATES PATENTS

3,671,411	6/1972	Ray et al.	204—130
3,657,082	4/1972	Wells et al.	204—130

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PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,832,297 Dated August 27, 1974

Inventor(s) J. T. Paul (Case 10)

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Table I, in the heading of the fifth column, " boli " should read -- boil --.

Column 4, line 52, " shown " should read -- known --.

Column 4, line 67, " throughout " should read -- throughput --.

Column 5, line 46, " 77 " should read -- 37 --.

Signed and sealed this 5th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents