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Duffy

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[54] **TREATMENTS FOR IMPROVING THE PROCESS AND YIELD OF CARBON FIBERS OBTAINED FROM THE PYROLYSIS OF RAYON YARN**

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[52] **U.S. Cl.** ..... **8/116 P**, 8/125, 8/130.1

[51] **Int. Cl.** **D06m 1/00**

[58] **Field of Search** ..... 8/125, .116 P, 130.1, 131

[56] **References Cited**

UNITED STATES PATENTS

2,743,232 4/1956 Chance et al. ..... 8/116 P

Primary Examiner—Stephen J. Lechert, Jr.

Attorney, Agent, or Firm—R. S. Sciascia; J. A. Cooke

[57] **ABSTRACT**

A method of treating cellulosic yarn, prior to carbonization and graphitization, which comprises treating said yarn with either bis (chlorodiphenylphosphine) decaborane or dimeric chlorophospha (III)-o-carborane so that the cellulose reacts with these compounds.

26 Claims, 2 Drawing Figures

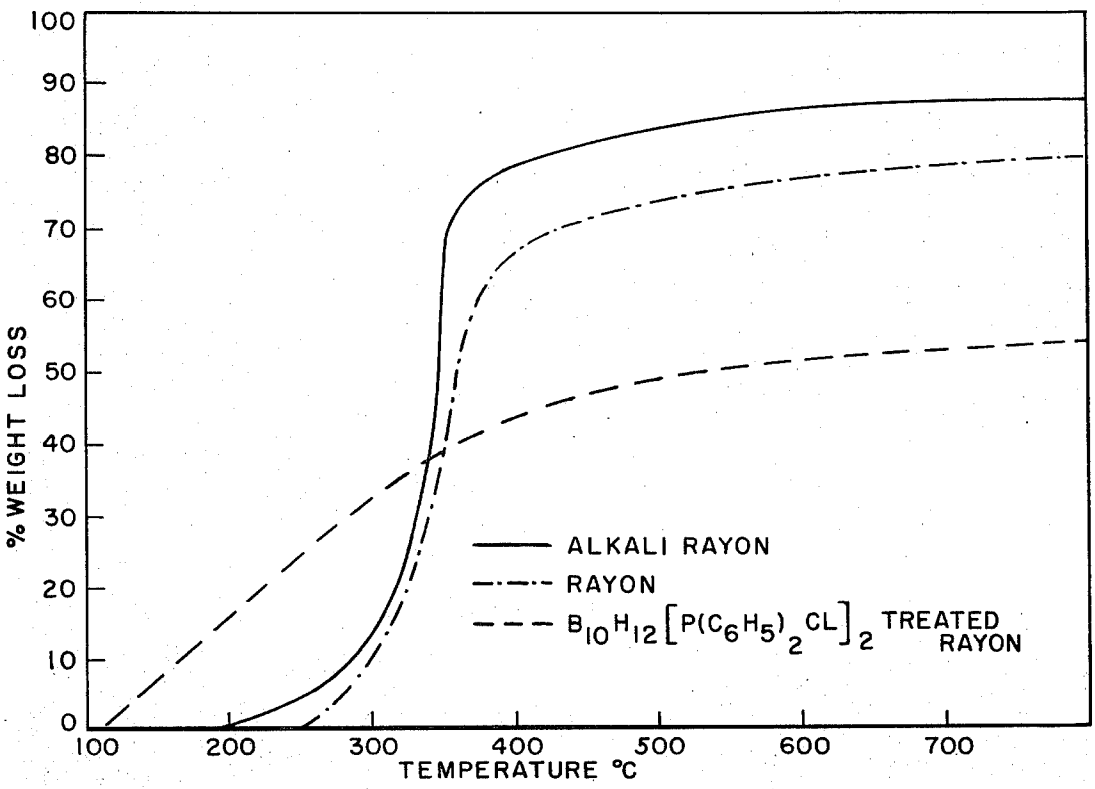

100
90
80
70
60
50
40
30
20
10
0
% WEIGHT LOSS
100
200
300
400
500
600
700
TEMPERATURE °C
ALKALI RAYON
RAYON
$B_{10}H_{12}[P(C_6H_5)_2CL]_2$ TREATED RAYON

FIG. 1.

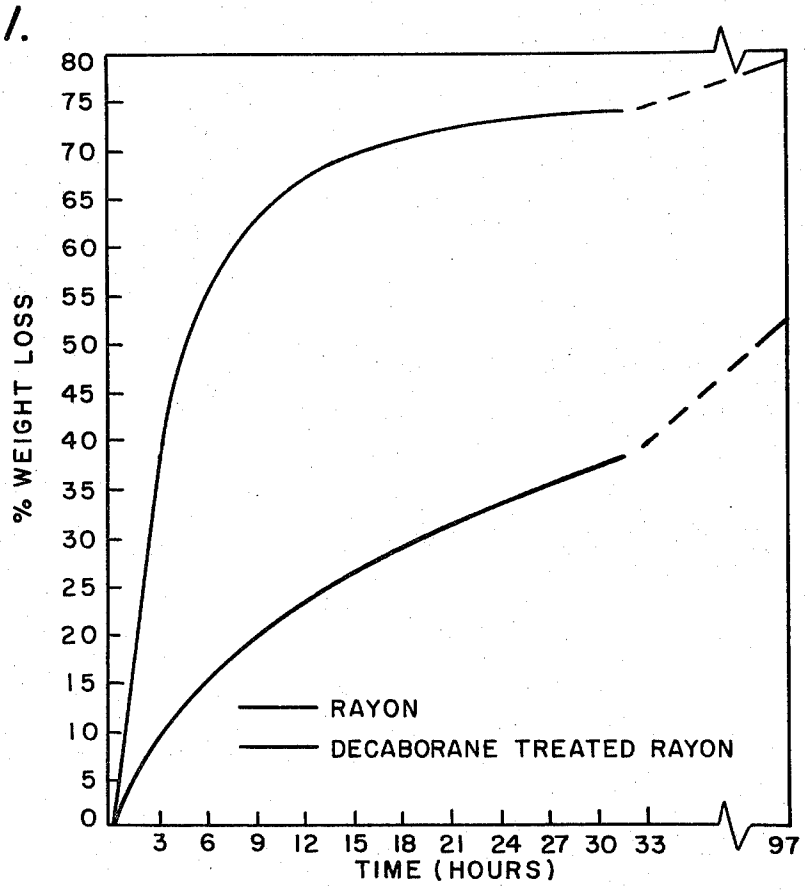

80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
% WEIGHT LOSS
3
6
9
12
15
18
21
24
27
30
33
97
TIME (HOURS)
RAYON
DECABORANE TREATED RAYON

FIG. 2.

TREATMENTS FOR IMPROVING THE PROCESS AND YIELD OF CARBON FIBERS OBTAINED FROM THE PYROLYSIS OF RAYON YARN

BACKGROUND OF THE INVENTION

The development of high strength-high modulus graphite fibers from rayon and other cellulosic fibers began in this country in the early 1950's. Rayon yarn is the most preferable because of its availability, low cost, and nonmelting character. Fibers of graphite have been formed by reducing the cellulosic materials to a carbon constituent at extremely high temperatures. While a number of methods of graphitization have been used, one of the more common processes involves three distinct stages: (1) preoxidation in air at low temperatures, (2) carbonization up to 1300° C., and (3) graphitization under tension at 2800 – 3000° C.

The beginning precursor yarn should have a high carbon content and the carbonization process should yield as high a weight retention as possible.

The resulting graphitized form of carbon has been widely used in high temperature applications. Although lower in tensile strength than other materials, they may be made to have improved flexural characteristics and may easily be integrated into composite bodies. Further, the sublimation point of graphite is very high, and the material is resistant to many types of corrosive attack. It may thus be used in many ways and for many purposes. Graphite fibers are light in weight, flexible, inert for most purposes, and have strength characteristics which increase with temperature. Fabrics alone may be used as filters in chemical processes, or as lining and fire walls, or in industrial processes where corrosive hot gases destroy other materials. Bonded or molded composite structures may be employed wherever high heat stresses are encountered. Furthermore, from the standpoint of erosion resistance, graphite and graphite molding compounds have potentials superior to most other materials. They may be used at points of extreme thermal stress, such as constricted areas of rocket engine nozzles and exit cone inserts.

As mentioned above, the graphitization of cellulosic yarn, such as rayon, is carried out in three distinct stages. Stage 1 involves low-temperature pyrolysis of cellulose. This low temperature pyrolysis causes random dehydration of hydroxyl groups, producing dehydrocellulose, which is the principal source of char at elevated temperatures. However, a second pyrolysis competes with this dehydration reaction, leading to the formation of volatile levoglucosan. Since volatization of levoglucosan and its degradation product produces large weight losses and tars as the decomposition temperature is raised, and formation of levoglucosan results in a lower char content in the graphitized fiber, any conditions which favor the dehydration reaction over the formation of levoglucosan are desired. Various methods in the past have been directed to such a result, such as the method of U.S. Pat. No. 3,479,150. It is noted that the purpose of a first stage, prior to carbonization, is to stabilize the yarn so that one avoids the formation of a tar and possible ignition of rayon fibers during heating. Tar is to be avoided since it will bind the fibers together and eventually create a locking effect, reducing the tensile strength.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to produce a graphite yarn of high char.

It is another object of this invention to convert a cellulosic yarn to a graphite yarn with as high a weight retention as possible.

It is still another object of the instant invention to obtain a carbonized fiber which is inherently strong and flexible.

It is yet another object of the subject invention to produce a carbonized yarn showing no signs of filament fusion.

It is a further object of this invention to produce a cellulosic yarn having a high oxidative stability and a slower rate of initial weight loss when subject to a pyrolysis treatment.

These and other objects are accomplished by the present invention, wherein the cellulosic yarn is treated with either chlorophospha (III)-o-carborane [hereinafter DCPC] or bis (chlorodiphenylphosphine) decaborane [hereinafter BCDPD], prior to the carbonization procedure.

Other objects, advantages and novel features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings wherein FIG. 1 represents a thermogravimetric anaylsis of rayon treated with bis (chlorodiphenylphosphine) decaborane (BCDPD) and FIG. 2 is a graph showing the isothermal weight loss in air at 250° C. of rayon treated with BCDPD.

BRIEF DESCRIPTION OF THE DRAWINGS

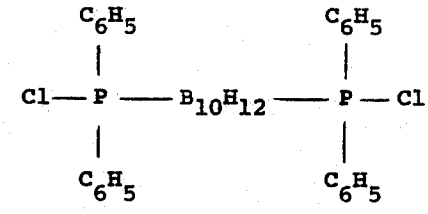
FIG. 1 is a plot of percent weight loss against temperature, for rayon, alkali rayon and BCDPD treated rayon.

FIG. 2 is a plot of time against percent weight loss in air for rayon and BCDPD treated rayon.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

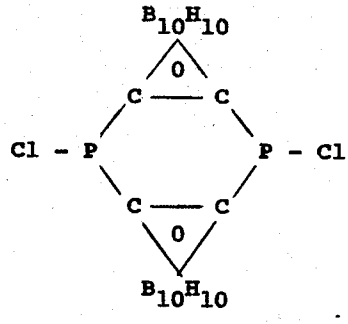
It has been found that the above-desired results can be achieved by reacting the cellulosic yarn, which will preferably be rayon, but can be any cellulose containing yarn such as cotton, linen, kemp, jute, flax, wood, etc. with either of two borane compounds.

The first compound is BCDPD, which is



and is more fully described in U.S. Pat. No. 3,203,984, issued Aug. 31, 1965, to Schroeder et al., wherein a suitable method of preparation is set forth. This material can be readily purchased from the Olin Corporation.

The other material, which can also be purchased from the Olin Corporation, is DCPC, and can be represented as



This compound is more fully described, as is its method of preparation, in U.S. Pat. No. 3,373,193, issued Mar. 12, 1968, to Alexander et al.

The treatment is designed to effect reaction between the cellulose and the compound. Some type of swelling treatment is required to insure reaction of the fibers. Thus, the reaction is generally carried out by: (1) a mercerization treatment, to swell the fibers, for a period of about 1 to 15 minutes, followed by; (2) a water washing for about 15 to 35 minutes, followed by; (3) a soaking of the yarn in pyridine so as to replace the water in the yarn with pyridine; and finally (4) treatment of the yarn with a treatment solution so as to effect reaction of the swollen fibers.

The initial mercerization treatment is a conventional process, familiar to those skilled in the textile treating art. Generally, any standard base such as an alkali metal or alkaline earth metal hydroxide is used in concentrations which can vary from about 1 percent to about 30 percent of the basic solution. The concentration of base will, of course, depend on the deleterious effects that the base has on a particular yarn. For example, when rayon yarn is treated with more than a 6 percent sodium hydroxide solution, a weak yarn, showing partial fusion of the monofilaments, was obtained, while a 6 percent alkali rayon is soft and flexible. Thus, when rayon is used as the yarn, an alkali concentration of 6 percent is the maximum weight percentage tolerable. When another type of yarn is used, a preferred weight percentage of alkali would be about 20 weight percent.

It is noted that the conversion of rayon to alkali rayon in the mercerization step has an adverse effect on thermal decomposition properties. The temperature of initial decomposition for alkali rayon is about 50° C. lower than that of untreated rayon, and the final weight retention of alkali rayon at 800° C. is only 13 percent compared to 20 percent for untreated rayon. This decrease can be explained by the fact that, in the swollen condition, alkali rayon is subject to depolymerization caused by air oxidation. The result is that any chemical treatment which requires swelling in caustic to insure reaction suffers a weight loss penalty on pyrolysis. In spite of this, the beneficial char improvements, obtained because of increased reaction of the fibers in the swollen condition, warrant the use of a mercerization type treatment prior to the reaction.

Following the mercerization treatment, which results in an increase in the fiber cross section and a corresponding decrease in the fiber length, the yarn is washed with water, then press dried to remove the bulk water, and then soaked in pyridine so that the pyridine can replace as much water as possible in the yarn. A suitable treatment is to wash with water for about 10 to 50 minutes, press dry to remove the bulk water, soak in pyridine for 10 to 30 minutes, press dry again and place in pyridine for another 5 to 20 minute soak.

After removal from the pyridine, the yarn is pressed and placed in a treatment solution. The treating solution comprises either of the two specific chemical compounds of the instant invention dissolved in a suitable solvent, such as pyridine. The temperature of the treating solution during treatment can be anywhere between room temperature and the boiling point of said solvent. Any solvent which is miscible with water but can also dissolve the specific compounds can be used. Such a solvent can also be used in the prior step of replacing water with pyridine, wherein the pyridine is replaced with said solvent. The total weight of the treating agent present in the solution is always about 2 to 3 times the amount required for a predetermined pickup on the yarn. The percent loading on the yarn has an effect on the pyrolysis behavior of the treated yarns. Using BCDPD on rayon as an example, weight retentions of 42 – 47 percent were obtained with loadings of 18 percent, 22 percent, and 33 percent, while 3 percent and 5 percent loadings produced retentions of only 15 percent and 19 percent, respectively, at 800° C., as compared to 20 percent for untreated rayon. The reason for the increased weight loss in the latter two cases as compared to untreated rayon, is the result of air oxidation of the alkali rayon. Thus, it is generally preferable to load the yarn with about 15 to 35 percent of the compound based on the weight of the yarn, remembering that values outside this range still provide an operative, although less preferable, process. It is most preferred to use a load of about 20 percent. The percent weight pickup is calculated by weighings before and after treatment. The treatment time is anywhere from 10 to 60 minutes, as 15 minutes is generally sufficient. The treated yarn is air dried and then vacuum dried.

The above procedure is best illustrated by the following Example, which is not meant, in any way, to limit the scope of the present disclosure or the claims to follow.

EXAMPLE I

Villwyte 1650/720 yarn was supplied by Midland-Ross Corporation of Cleveland, Ohio. The yarn was a two-ply, 720 filament/rayon ply yarn having a denier of 1650. The yarn, as received, contained a hydrocarbon lubricant, which was removed by continuous extraction with trichloroethylene followed by ethyl alcohol. The pyridine used was "Baker Analyzed" reagent grade.

The procedure used to treat Villwyte with the boron-phosphorus compounds was an adaptation of that reported by Schwenker and Pascu, in Ind. Eng. Chem. 50, 91 (1958). A continuous length of yarn (1 to 100 meters) was stretched between two bars and tied at the ends exactly 1 meter apart. The yarn was then immersed in a 6 percent sodium hydroxide solution without tension for a period of 1 minute. The mercerization process resulted in an increase in the fiber cross section and a corresponding decrease in the fiber length. Mercerization was terminated by washing with water for a period of 30 minutes. After press drying to remove the bulk water, the yarn was placed in pyridine and soaked for a period of 15 minutes. The yarn was press dried again and placed in fresh pyridine for another 10 minute soak. At this point, it was assumed that the pyridine had replaced most of the water in the yarn bundle.

After removal from the pyridine, the yarn was pressed and placed in a 10 percent treatment solution at 25° C. The total weight of the treating agent present in the solution was always two or three times the amount required for a 20 percent pickup based on the weight of the yarn used. The treatment time was 15

minutes and, after light pressing, the yarn was stretched under tension while air drying. Finally, the yarn was vacuum dried for 2 hours at 100° C. The shrinkage caused by the treatment was determined by measuring the distance between the ties which originally were placed 1 meter apart. Shrinkage amounted to 10 percent to 15 percent by this process. The percent weight pickup was calculated by weighings before and after treatment.

The thermogravimetric analysis (TGA) equipment used in this study was described in detail by Anderson, in J. Appl. Polym. Sci., 6, No. 22, 484 (1962). The treating solution was a 10 percent solution of BCDPD in pyridine. The thermal decomposition behavior is entirely different from that of the untreated yarn (FIG. 1). Decomposition starts at 100° C. for the treated yarn, which is 150° C. below that for untreated rayon, but the rate of initial weight loss is slower for the treated yarn. The final weight retention increases from 20 percent for untreated rayon to 47 percent for the BCDPD treated yarn at 800° C. Elemental analysis of the residue (Table I) shows a carbon content of 54.69 percent, which means that the actual weight retention of elemental carbon after pyrolysis was 26 percent. An additional undetermined quantity of carbon probably complexes with the 7.57 percent boron present in the residue. While no quantitative mechanical data was obtained on the carbonized yarn, it was inherently strong and flexible and maintained these properties after heating to 2250° C. There were no signs of filament fusion.

TABLE I

Elemental Analysis of Residues from the Pyrolysis of Bis(chlorodiphenylphosphine)decaborane (BCDPD)-Treated Rayon

NaOH used in mercerization, %	Loading of BCDPD on Rayon, wt-%	Residue at 800° C., %	Residue analysis				Carbon in residue at 800° C., %
			C, %	H, %	B, %	P, %	
6	11.8	34.7	68.14	1.46	3.82		23.6
6	16.5	37.6	61.71	1.61	9.04	1.65	23.2
6	21.0	47.0	54.69	1.58	7.57		25.7
10	—	33.0	79.14	1.26	4.22	1.65	26.1
16	—	35.0	79.36	1.17	4.29		27.8

The effect of air oxidation on BCDPD-treated yarns is important since, as was indicated previously, commercial graphite fiber producers subject the rayon precursor to a preoxidation treatment. Results at 250° C. in air (FIG. 2) show a more gradual loss of weight for the treated yarn. After 8 hours, untreated rayon had lost 62 percent of its weight while the BCDPD-treated rayon had lost only 19 percent. Final losses after 97 hours were 79 percent untreated and 52 percent treated. Thus, it appears that this treatment is of use in preventing excessive weight losses during the preoxidation step of the graphitization process.

EXAMPLE II

Example I is simulated using DCPC in place of BCDPD. The TGA results for the DCPC-treated yarn show an initial weight loss similar to that of the BCDPD treatment and a final weight retention of 53 percent at 800° C.

In both of the above treatments, it was found that extended periods of swelling would yield a stiff, brittle yarn, which was not suitable for carbonization. In both Examples, the pyrolyzed yarns were strong and flexible and showed no signs of filament fusion.

The fibers resulting from the above process can be used in a subsequent carbonization or graphitization process, and the resultant fiber will have an improved char yield and weight retention. In addition, the presence of boron in the char residue will permit the graphitization process to be carried out at a lower temperature since boron has been shown to perform as a catalyst for the graphitization process. Finally, since the treated yarn has a substantially increased oxidative stability at 250° C., this treatment might be used in the older oxidation method to help decrease the weight loss during this preoxidation process.

Various changes, modifications, alterations and substitutions can be made in the present method, its steps and parameters and in the equipment for carrying out the steps. All such modifications, changes, alterations and substitutions, as are within the scope of the appended claims, form a part of the present invention.

What is claimed is:

1. A process for modifying the properties of cellulosic yarn comprising treating said yarn with a solution of a compound selected from the group consisting of bis(chlorodiphenylphosphine)decaborne and dimeric chlorophospha (III)-o-carborane, in order to react the compound with the yarn.

2. A process according to claim **1** wherein said solution comprises pyridine as the solvent for said compound.

3. A process according to claim **2** wherein said yarn is treated with said solution at a temperature from about room temperature up to the boiling point of said pyridine.

4. A process according to claim **3** wherein the amount of said compound present in said solution is from about two to three times the amount necessary to load said yarn with from about 15 to about 35 percent of said compound, based on the weight of said yarn.

5. A process according to claim **4** wherein said yarn is rayon.

6. A process according to claim **5** wherein said compound is bis(chlorodiphenylphosphine) decaborane.

7. A process according to claim **5** wherein said compound is dimeric chlorophospha (III)-o-carborane.

8. A process for modifying the properties of cellulosic yarn comprising:

swelling the fibers of said yarn by mercerizing said yarn in a basic mercerizing solution; and then treating said yarn with a treating solution of a compound selected from the group consisting of bis(-chlorodiphenylphosphine) decaborane and dimeric chlorophospha (III)-o-carborane, in order to react the compound with the yarn.

9. A process in accordance with claim 8 wherein said basic mercerizing solution comprises from about 1 to about 30 weight percent of an alkali metal or alkaline earth hydroxide.

10. A process in accordance with claim 9 wherein said standard basic mercerizing solution comprises from about 1 to about 6 percent of sodium hydroxide.

11. A process in accordance with claim 9 wherein said treating solution comprises pyridine as the solvent for said compound.

12. A process in accordance with claim 11 wherein said yarn is treated with said treating solution at a temperature from about room temperature up to the boiling point of said pyridine.

13. A process in accordance with claim 12 wherein the amount of said compound present in said treating solution is from about two to three times the amount necessary to load said yarn with from about 15 to about 35 percent of said compound, based on the weight of said yarn.

14. A process according to claim 13 wherein said yarn is rayon and said standard basic mercerizing comprises from about 1 to about 6 weight percent of sodium hydroxide.

15. A process according to claim 14 wherein said compound is bis(chlorodiphenylphosphine) decaborane.

16. A process according to claim 14 wherein said compound is dimeric chlorophospha (III)-o-carborane.

17. In a process for the graphitization of cellulosic yarn, the improvement which comprises subjecting said yarn to a treatment prior to graphitization, wherein said treatment comprises:

swelling the fibers of said yarn by mercerizing said yarn in a basic mercerizing solution; and then treating said yarn with a treating solution of a compound selected from the group consisting of bis(-chlorodiphenylphosphine) decaborne and dimeric chlorophospha (III)-o-carborane, in order to react the compound with the yarn.

18. A process in accordance with claim 17 wherein said standard basic mercerizing solution comprises from about 1 to about 30 weight percent of an alkali metal or alkaline earth hydroxide.

19. A process in accordance with claim 18 wherein said standard basic mercerizing solution comprises from about 1 to about 6 percent of sodium hydroxide.

20. A process in accordance with claim 18 wherein said treating solution comprises pyridine as the solvent for said compound.

21. A process in accordance with claim 20 wherein said yarn is treated with said treating solution at a temperature of from about room temperature up to the boiling point of said pyridine.

22. A process in accordance with claim 21 wherein the amount of said compound present in said treating solution is from about two or three times the amount necessary to load said yarn with from about 15 to about 35 percent of said compound, based on the weight of said yarn.

23. A process according to claim 22 wherein said yarn is rayon and said standard basic mercerizing comprises from about 1 to about 6 weight percent of sodium hydroxide.

24. A process according to claim 23 wherein said compound is bis (chlorodiphenylphosphine) decaborane.

25. A process according to claim 23 wherein said compound is dimeric chlorophospha (III)-o-carborane.

26. The process of claim 23 wherein the treatment comprises mercerizing to swell the yarn for about 1 to 15 minutes, washing the yarn in water for about 15 to 35 minutes, soaking the yarn in pyridine to replace the water in the yarn with pyridine, and treating the yarn with the treating solution.

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