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PROCESS FOR CARBONIZING FIBROUS MATERIALS

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ABSTRACT OF THE DISCLOSURE

A process for improving the thermal carbonization of carbon-containing substrates comprising treating said substrates prior to carbonization with at least a catalytic amount of a catalyst selected from esters of phosphoric acid, esters of phosphorothioic acid, phosphoramidic acids, alkylphosphoramidic acids, alkylphosphonic acids alkylphosphonothionic acids, and phosphonitrile amide derivatives, and heating said treated substrates until a carbonized product having a carbon content of at least 50% by weight carbon is produced.

This invention concerns reagents useful as catalysts for the pyrolytic transformation of carbon-containing substrates to carbon products.

More particularly, this invention relates to novel catalysts employed during the carbonization and graphitization of cellulosic substrates to effect product and process improvement.

Carbonization as used herein refers to thermally actuated processes which transform a carbon-containing substrate to a carbon product. These carbon products include both carbon and graphite materials whose carbon (or graphite) content ranges from about 50% by weight to almost 100% by weight.

The term cellulosic as used herein refers to substrates comprising natural cellulose or its modified derivatives. These include cotton, linen, hemp, jute, flax, wood, cuprammonium rayon, viscose and the like. These cellulosics can be employed unblended or in the form of blends with non-cellulosic materials. The latter include, but are not limited to the acrylics, polyesters, and polyamides. The substrates can be used in the form of their yarns, fibers, or threads as well as in the form of materials such as woven cloths, knitted fabrics, webs, laminates, or any other fabricated form utilizing textile fabricating processes.

The carbonization of carbon-containing substrates to produce carbon or graphite fllaments dates back more than sixty years. More recently, simulated by the need in the aerospace program for strong, lightweight and inert materials, there has been a resurgence of carbonization and graphitization research. Particularly of interest are programs in which carbon-containing textile materials such as cellulosic yarn and cloth have been pyrolyzed under carefully controlled conditions to produce carbon products retaining a substantial portion of the desirable characteristics of the original textile substrate. For example, the products are lightweight, have good flexibility, and are non-toxic. Further, as compared to the original cellulosic substrate, they have improved chemical inertness and dimensional stability. Finally, in contrast to the cellulosics, they possess outstanding resistance to flammability and good high-temperature ablation.

Most of the published procedures for carbonizing cellulosics disclose lengthy stepwise heating processes to produce the final product. Initially, the substrate is slowly heated to temperatures ranging from about 200° C. to 300° C. followed by a final and brief heating step at high

temperatures ranging from about 550° C. to 2000° C. or even higher. Not only are equipment and labor costs high but the prolonged heating at elevated temperatures reduces yields and requires the use of inert atmospheres to prevent combustion of the substrate. As a result of these factors, the cost of carbonized articles is exceedingly high and the widespread use of the carbon products has been kept to a minimum.

It has been known for some time that pretreatment of the cellulosic substrate with appropriate catalytic reagents can reduce the time required for completion of the carbonization cycle. Recently, the use of certain mineral acids and acidic salts such as phosphoric acid and diammonium hydrogen phosphates as carbonization catalysts have been described in patents (U.S. 3,235,323 and 3,305,315). The patentees have indicated that the use of these catalysts during carbonization produces improved carbon products compared to products obtained without catalysts. However, even when a superior catalysts such as diammonium hydrogen phosphate $[(NH_4)_2HPO_4]$ is used, difficulties are encountered. For example, even when the catalyst is used, a comparatively lengthy heating cycle is required to obtain a carbonized product having acceptable properties. Further, diammonium hydrogen phosphate should be applied at near boiling temperatures. A major advance in the art would be the development of new catalytic reagents which could be applied at moderate temperatures (20° C.–50° C.) and which would substantially reduce the heating time required for carbonization compared to diammonium hydrogen phosphate. In addition, a truly superior catalyst would lend itself to simple, routine application techniques and would produce a carbon product having improved physical properties in good yield. In addition, the catalyst should be relatively simple to prepare and purify, and would function at effectively low concentrations.

It is, therefore, an object of this invention to disclose a novel and superior class of catalysts for the carbonization of cellulosic substrates.

A more particular object of this invention is the development of carbonization catalysts which substantially reduce carbonization time compared to presently utilized catalysts such as diammonium hydrogen phosphate.

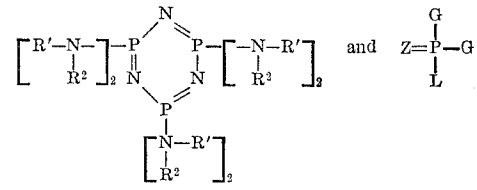
Another specific object of this invention is the development of novel water-soluble carbonization catalysts which readily lend themselves to simplified application procedures conducted at moderate temperatures.

An additional specific object of this invention is the utilization of the inventive catalysts to prepare carbon products having improved properties.

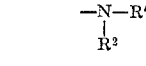
Other objects of this invention will become apparent to those skilled in the art after a reading of this application.

The above objects are realized by the treatment of a cellulosic substrate prior to complete carbonization with a class of carbonization catalysts to be described more fully below.

In practice, a cellulosic substrate is treated with one or more catalysts selected from the groups consisting of:



wherein G is selected from the group consisting of —OR or



R is an alkyl radical having from 1 to 4 carbon atoms, R' and R^2 which can be the same or different at any given time are selected from hydrogen and R; L is selected from the group consisting of alkyl radicals containing from 1 to 4 carbon atoms, halogenated alkyl radicals containing from 1 to 4 carbon atoms, and G; and Z is selected from the group consisting of oxygen and sulfur; in an amount sufficient to incorporate at least a catalytic quantity [1] of catalyst into the substrate to be carbonized.

While the above two classes of compounds provide satisfactory catalysts for the carbonization of carbon-containing substrates, in any large group for various reasons some members of the group are preferred to others. In the instant case the preferred catalyst are selected from the group consisting of phosphoric triamide, phosphorothioic triamide, phosphonitrile amide cyclic trimer, diethyl methylphosphoramidate, and diethyl ethylphosphoramidate. These compounds are the preferred catalysts for carbonizing carbon-containing substrates because they reduce the carbonization time required in the first heating stage and produce carbon products having outstanding properties in most instances in high yield.

A secondary favored group of compounds which, while excellent catalysts, are not as outstanding as the preferred catalysts, are those compounds selected from the group consisting of methylphosphonic diamide and and (chloromethyl)phosphonothionic diamide. These catalysts generally give good yields of carbonized products and the products have superior properties. The trialkyl phosphates as exemplified by triethyl and trimethyl phosphate, N,N',N''-trimethylphosphoric triamide, and diethyl isopropylphosphoramidate, form a tertiary group of very good catalysts which give lesser yields of a product having somewhat less desirable properties.

The residium of the compounds included within the two broad classes of catalysts are least preferred for a variety of reasons including poor water solubility, poorer properties, and the requirement for longer residence times.

After treatment with catalysts, the treated substrate is then heated to effect removal of the volatiles to obtain a permanently dehydrated material having a carbon content of at least 50% by weight carbon. This black appearing, devolatilized and heat-treated material can be utilized as an electrical insulator or can be further heated to produce a carbonized or graphitized material having a carbon content of at least 85% and up to 100% by weight carbon. The latter products are useful as electrically conductive materials and when utilized in resin-bonded laminates are exceedingly valuable in fabricating ablative composites.

In the preferred practice, a fibrous cellulosic textile substrate such as cotton or rayon cloth or yarn is treated with an aqueous solution (1–10% active solids) of at least one catalyst selected from the above-described, preferred group until a pickup of 150–300% based on the dry weight is obtained. The treated cellulosic substrate is dried to a moisture content of approximately 8-12% and heated at 200–300° C. until a black fibrous substrate having a carbon content between 50–65% by weight carbon is produced. Ordinarily, depending upon the heating temperature, and the efficacy of the catalyst, the initial carbonization takes between 3 and 12 minutes. Substrates treated with diammonium hydrogen phosphate require between 8–12 minutes when carbonized at this temperature range.

As noted earlier, the product containing 50–60% by weight of carbon can be further carbonized to produce a product containing 85% by weight or higher carbon content. This is most easily accomplished by heating the carbonized substrate briefly above about 1000° C. in a non-oxidizing atmosphere. The upper temperature range

[1] While a catalytic quantity of catalyst is a variable depending upon the catalyst and reaction conditions employed, in general this quantity varies between 2 and 30% by weight of catalyst(s), based on the weight of the substrate.

is primarily limited by whether a carbon or graphite product is desired. The precise residence time required for the final carbonization is a variable depending primarily on the second carbonization temperature and to some extent on the catalyst employed during carbonization. When phosphoric triamide (one of the preferred catalysts of this invention) is employed as catalyst, good results have been obtained by heating the black uniformly lustrous fibrous substrate for from 20 to 120 seconds at the 1300° C.–1500° C. range. After the final carbonization (or graphitization) is complete the fibrous carbon product is cooled, collected and scoured or otherwise finished depending upon the intended end use.

As described supra, the preferred carbon-containing substrates are cellulosics, particularly those broadly described as regenerated cellulose or rayon. The fibrous rayon can be in the form of a cloth (woven, knitted or felted), non-woven random layed fibrous or needle-punched batts, felts, fabrics or tissues formed of staple, fibers, yarns, rovings, continuous filament tows and the like.

The cellulosic substrate can be in the form of yarns, fibers or filaments (or the textile fabrics made from these) whose diameter can vary widely. An especially suitable range lies between about 5 to about 30 microns in diameter.

As the preferred catalysts of this invention are water soluble, it is most convenient to utilize the one or more catalyst employed in the form of their aqueous solutions. Water solubility is an important attribute of a preferred catalyst since it permits the use of simple application techniques and existing apparatus. However, if desired, emulsions or suspensions of the soluble or less soluble catalyst(s) in non-aqueous solvents or mixtures of non-aqueous solvents with water can be employed. Textile adjuvants such as surfactants, emulsifiers, stabilizers, or the like can be present in the treating solution if desired.

The mode of applying the treating solution is not critical to the success of this invention. Any application technique utilized in the textile art can be employed. These include, but are not limited to, padding, brushing, spraying, coating, and the like. As the catalysts can be applied at moderate temperatures, a convenient mode of applying them to yarn is to run the yarn continuously through an aqueous bath containing catalyst and removing excess solution to achieve the desired wet pickup. When cloth is used as the substrate, comparable application methods may be employed.

After the application is complete the treated substrate is dried. The drying step can be air dried or heat assisted. It can be conducted as a separate step or can be incorporated as part of the heating cycle.

Similarly the carbonization or graphitization can be conducted in two or more stages or as a continuous stage. No special heating source is needed. Conventi onal muffle or tube furnaces can be used modified or as marketed.

In the initial carbonization phase (up to about 50–60% by weight carbon content) the use of the inventive catalysts precludes the need for heating in a non-oxidizing atmosphere to prevent combustion. However, the subsequent high temperature heating step where the carbon content runs from 85% by weight and higher requires a non-oxidizing atmosphere (less than 10% by weight oxygen). This can be accomplished by heating the substrate in a nitrogen, carbon dioxide, or noble gas atmosphere (or mixtures thereof) or by diluting air with diluents such as steam, ammonia, or the above enumerated inert gases until the desired environment is obtained.

The final carbonized or graphitized carbon product can be washed or scoured to remove undesirable contaminants or salts if desired. In the former case the product can be batchwise or continuously immersed in water while in the latter instance soaps or detergents can be added to the bath if convenient.

Having described the inventive process generally, it only remains to disclose specific embodiments of the use of the catalysts of this invention in carbonization and graphitization procedures. A description of the evaluation techniques precedes the specific embodiments.

(I) CRITERIA USED TO EVALUATE THE CARBONIZATION CATALYSTS OF THIS INVENTION

In order to evaluate the carbonization catalysts objectively and to compare them in efficacy to the prior art standard (diammonium hydrogen phosphate), the following criteria were used:

(A) Length of time required to carbonize satisfactorily to a carbon product when the first stage of carbonization is carried out at a relatively low temperature, i.e., about 260° C.

(B) Tensile strength of the substantially carbonized (85% carbon or over) yarn.

(C) Modulus of elasticity of the substantially carbonized yarn.

(D) Percent by weight carbon content of the substantially carbonized product.

(E) Electrical resistivity of the substantially carbonized yarn.

In all instances, diammonium hydrogen phosphate was used as the control.

(A) Specific two-stage carbonization process used

(1) A viscose yarn continuous filament yarn (1650 denier/720 filaments/2Z) manufactured by the IRC Division of Midland Ross Corporation was used as substrate. The yarns were usually two-piled and treated with the catalyst being evaluated by running the yarn through a 3–10% by weight aqueous solution of the catalyst so that wet pickup of 200% (based on dry weight) is obtained.

(2) The treated yarn is dried in the presence of air at about 120° C. for 10 minutes to produce a treated substrate containing about 8–10% by weight moisture.

(3) The above yarn, which is at its normal moisture regain, is heated in the presence of air at about 260° C.[2] for a sufficient period of time to produce a partially carbonized substrate whose carbon content ranges between 50–65% by weight carbon.

(4) The partially carbonized substrate is further carbonized in a nitrogen atmosphere at 1372° C. for 20 seconds to produce a substantially carbonized substrate having a carbon content of about 90% by weight or higher.

(5) The carbonized yarn is collected and wound on an appropriate storage cone.

(B) Tensile strength

(1) A 60-inch length sample of the aforedescribed viscose yarn which has been carbonized is taken for sampling. Samples of both the 50–60% by weight and 85–100% by weight carbon content are used. Both samples are conditioned for 16 hours at a relative humidity of 65±2% (at 21° C.±1° C.). The sample is tested on an Instron Tensile Tester (manufactured by Instron Engineering Corp.) as follows: The sample is positioned so that the span between the jaws of the instrument is five inches. The rate of extension is 10% per minute and the chart speed adjusted so that every inch on the chart equals ½% extension. The ultimate breaking strength in grams is calculated from the chart and used to calculate the tensile strength figure.

(2) Ultimate elongation (strain)—Using the chart, the ultimate elongation value is determined.

(C) Modulus of elasticity

Using the slope of the curve obtained in the tensile strength determination, the modulus, expressed in grams per denier, is determined.

[2] Where other temperatures were used, they are indicated.

(D) Carbon content

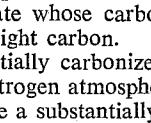
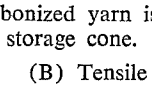
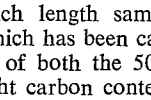
A 3–4 mg. sample of carbon yarn, previously dried and pulverized, is weighed out in an aluminum combustion boat and introduced into a combustion tube of a Coleman Model 33[3] Carbon-Hydrogen Analyzer. The combustion tube is maintained at 900° C. during ignition. The analyzer is previously calibrated against a sample of chemically pure acetanilide. All samples are run in duplicate.

(E) Electrical resistivity

A resistance meter capable of measuring resistance below approximately 50,000 ohms is used. A 2.5 centimeter span of carbonized yarn having a content between 85–100% by weight carbon is used as sample. The sample is removed and tested immediately after carbonization. Three readings are taken over the span of the yarn and these readings are averaged to give the resistance figure expressed in ohms per centimeter. The resistance value and the cross sectional area are used to calculate the specific resistivity. A resistivity value of 20 ohm-cm. or less is considered satisfactory for carbonized yarns containing between 85–100% by weight carbon, all of the preferred catalysts produced yarns having resistivity values within this value.

(II) SOURCE OF CATALYSTS

All of the catalytic reagents of this invention but one[4] are known compounds. A description of the source of the prefered reagents is indicated below. Where the reagents were synthesized a reference to the literature or a description of the preparation is provided.

Catalyst	Source
Phosphorothioic triamide $SP(NH_2)_3$.	Synthesized according to the method described in Inorganic Syntheses, Vol. VI, pp. 111–112 (1960).
Phosphoric triamide $OP(NH_2)_3$.	Synthesized according to the method described in Chem. Ber., Vol. 87, p. 333 (1954).
N,N',N''-Trimethylphosphoric triamide $OP(-NH-CH_3)_3$.	Synthesized according to the method of Arceneaux et al., described in J. Org. Chem., Vol. 24, p. 1,420 (1959).
Phosphonitrile amide cyclic trimer 	Synthesized according to the method of Shaw and Ogawa described in Journal of Polymer Science, Part A, Vol. 3, pp. 3343–3351 (1965), where it was called "hexaaminocyclotriphosphazatriene". The systematic name is 2,2,4,4,6,6-hexaamino-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine.
Methylphosphonic diamide 	Synthesized according to the method of Ratz described in J. Am. Chem. Soc., Vol. 77, p. 4170 (1955).
(Chloromethyl)phosphonothionic diamide 	See preparation below: [1]

[1] A 5-liter reaction flask is charged with 3 liters of chloroform (dried over $CaCl_2$), and ammonia gas is bubbled into the solvent for 3 hours at −15°C. During the introduction of the ammonia, 183.4 g. (1.0 mole) of (chloromethyl) phosphonothioic dichloride is added dropwise to the flask at −15°C over a 2-hour period. After the addition of dichloride is completed the mixture is stirred at −15°C and ammonia is bubbled through for an additional one hour. The reaction mixture is then allowed to come up to room temperature overnight. The mixture is filtered and the white solid is collected and dried. The filtrate is evaporated and the residue combined with the collected solids. The combined solids are refluxed with a 75=25 chloroform-methanol mixture to extract the product. The extract on cooling gives white crystals which are collected and dried and the filtrate is used to extract more product to give a total of 116 g. of the product, (chloromethyl)phosphonothionic diamide in 66.5% yield, MP 107–109°C.. The analyses were as follows:

Elements	Calculated	Found
C	8.35	8.18
H	4.15	3.74
N	19.3	19.2
P	21.4	22.9

[3] Manufactured by Coleman Instruments, Inc., 42 Madison St., Maywood, Ill.

[4] (Chloromethyl)phosphonothionic diamide.

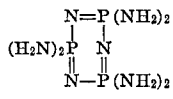
The following compounds used as catalysts were purchased from a commercial source:

Trimethyl phosphate	$OP(-OCH_3)_3$
Triethyl phosphate	$OP(-OC_2H_5)_3$
Diethyl methylphosphoramidate	$OP(-OC_2H_5)_2$ $\vert$ $HNCH_3$
Diethyl ethylphosphoramidate	$OP(-OC_2H_5)_2$ $\vert$ HNC_2H_5
Diethyl isopropylphosphoramidate	$OP(-OC_2H_5)_2$ $\vert$ $HNCH(CH_3)_2$

(III) EVALUATION RESULTS

Using the procedure described in Section I(A), the above compositions and mixtures thereof were evaluated as catalysts after carbonizing for the indicated time at the first heating stage of about 260° C.[5] Diammonium hydrogen phosphate in all instances was used as control. The results using yarn substrates were as follows.

(A) PHOSPHONITRILE AMIDE CYCLIC TIMER, (APPLIED AS 3.5% SOLUTION)



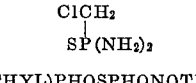
After carbonization for the specified times and temperatures the resultant yarn had the indicated properties.

	Carbonization temperatures		
	260° C.–1,372° C.		266° C.–1,372° C.
Residence times at lower temperatures	6 min.	5.25 min.	3.25 min.
Product properties:			
Denier	1,426	1,381	1,377
Breaking strength, grams	2,070	2,469	1,740
Tensile strength, g./d.[1]	1.45	1.79	1.26
Elongation, percent	1.36	1.46	1.48
Modulus of elasticity, g./d.	151	169	135
Carbon content, percent	92.5	93.1	90.0

[1] g.d.—grams/denier.

B. N,N',N''-TRIMETHYLPHOSPHORIC TRIAMIDE, $OP(-NH-CH_3)_3$ (APPLIED AS 3.5% SOLUTION)

	Carbonization temperatures	
	260° C.–1,372° C.	266° C.–1,372° C.
Residence times at lower temperatures	10.5 min.	8.4 min.
Product properties:		
Denier	1,110	1,189
Breaking strength, g./d.	1,887	1,370
Tensile strength, g./d.	1.70	1.15
Elongation, percent	1.26	.87
Modulus of elasticity, g./d.	156	165
Carbon content, percent	97.0	95.6



(C) (CHLOROMETHYL)PHOSPHONOTHIONIC DIAMIDE (APPLIED AS A 3.5% SOLUTION)

	Carbonization temperatures	
	260° C.–1,372° C.	
Residence times at lower temperature	8.4 min.	10.5 min
Product properties:		
Denier	1,220	1,201
Breaking strength, grams	2,250	2,358
Tensile strength, g./d.	1.42	1.96
Elongation, percent	1.10	1.57
Modulus of elasticity, g./d.	160	165
Carbon content, percent	97.5	95.0

[5] Where temperatures other than 260° C. were used they are indicated n the tables.

	Carbonization temperatures	
	266° C.–1,372° C.	
Residence times at lower temperature	8.4 min.	10.5 min.
Product properties:		
Denier	1,200	1,169
Breaking strength, grams	2,460	1,837
Tensile strength, g./d.	2.05	1.57
Elongation, percent	1.62	1.26
Modulus of elasticity, g./d.	167	146
Carbon content, percent	94.2	95.1

(D) Diammonium hydrogen phosphate, $(NH_4)_2HPO_4$ (applied as 5% solution)

Carbonization temperatures, ° C.	260–1372
Residence times at lower temperature, min.	11.6
Product properties:	
Denier	1160
Breaking strength, grams	1304
Tensile strength, g./d.	1.13
Elongation, percent	1.76
Modulus of elasticity, g./d.	150
Carbon content, percent	93.0

(E) Phosphorothioic triamide, $SP(-NH_2)_3$ (applied at 3.5% solution)

Carbonization temperatures, ° C.	260–1372
Residence times at lower temperature, min.	5.25
Product properties:	
Denier	1327
Breaking strength, grams	2250
Tensile strength, g./d.	1.71
Elongation, percent	1.42
Modulus of elasticity, g./d.	164
Carbon content, percent	94.8

(F) Phosphoric triamide, $OP(-NH_2)_3$ (applied as 3.5% solution)

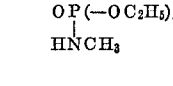
Carbonization temperatures, ° C.	260–1372
Residence times at lower temperature, min.	5.25
Product properties:	
Denier	1306
Breaking strength, grams	2186
Tensile strength, g./d.	1.66
Elongation, percent	1.46
Modulus of elasticity, g./d.	168
Carbon content, percent	93.6

G. TRIMETHYL PHOSPHATE, $OP(-OCH_3)_3$ (APPLIED AS A 5% SOLUTION)

	Carbonization temperatures	
	260° C.–1,372° C.	266° C.–1,372° C.
Residence times at lower temperatures	7 min.	4.2 min.
Product properties:		
Denier	910	890
Breaking strength, grams	1,834	1,334
Tensile strength, g./d.	2.02	1.50
Elongation, percent	1.24	0.85
Modulus of elasticity, g./d.	195	201
Carbon content, percent	95.8	93.0

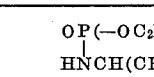
H. TRIETHYL PHOSPHATE, $OP(-PC_2H_5)_3$ (APPLIED AS A 3% SOLUTION)

	Carbonization temperatures		
	260° C.–1372° C.		266° C.–1372° C.
Residence times at lower temperatures	5.25 min.	4.9 min.	5.25 min.
Product properties:			
Denier	826	980	832
Breaking strength, grams	1,942	1,640	1,630
Tensile strength, g./d.	2.35	1.80	1.96
Elongation, percent	1.45	1.09	1.14
Modulus of elasticity, g./d.	192	196	205
Carbon content, percent	95.2	94.6	96.5



I. DIETHYL METHYLPHOSPHORAMIDATE, (APPLIED AS A 5% SOLUTION)

	Carbonization temperatures	
	254° C.–1372° C.	260° C.–1372° C.
Residence times at lower temperatures	4.2 min.	7 min.
Product properties:		
Denier	1,072	1,032
Breaking strength, grams	2,118	2,232
Tensile strength, g./d.	1.97	2.01
Elongation, percent	1.40	1.60
Modulus of elasticity, g./d.	183	175
Carbon content, percent	94.9	91.7

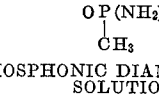


J. DIETHYL ETHYLPHOSPHORAMIDATE, (APPLIED AS A 5% SOLUTION)

	Carbonization temperatures		
	254° C.–1372,° C.	260° C.–1,372° C.	
Residence times at lower temperatures	7 min.	5.25 min.	3.5 min.
Product properties:			
Denier	900	816	1,012
Breaking strength, grams	2,490	2,452	2,178
Tensile strength, g.d.	2.77	3.00	2.15
Elongation, percent	1.69	1.83	1.61
Modulus of elasticity, g./d.	211	202	169
Carbon content, percent	99.6	98.7	95.2

(K) Diethyl isopropylphosphoramidate (applied as a 5% solution)

Carbonization temperatures, ° C.	260–1372
Residence times at lower temperature, min.	5.25
Product properties:	
Denier	830
Breaking strength, grams	1320
Tensile strength, g./d.	1.59
Elongation, percent	0.77
Modulus of elasticity, g./d.	245
Carbon content, percent	93.0



L. METHYLPHOSPHONIC DIAMIDE (APPLIED AS 3½% SOLUTION)

	Carbonization temperatures	
	271° C.–1372° C.	277° C.–1372° C.
Residence times at lower temperatures	7 min.	5.25 min.
Product properties:		
Denier	1,014	1,002
Breaking strength, grams	2,270	2,014
Tensile strength, g./d.	2.15	2.01
Elongation, percent	1.34	1.23
Modulus of elasticity, g./d.	204.7	210.8
Carbon content, percent	93.0	93.5

The results using fabric substrates are as follows:

(M) A woven fabric consisting of 1650/720/2Z rayon yarns in a 21 x 22 (warp x filling) construction was impregnated with a 3.5% by weight aqueous solution of N,N',N''-trimethylphosphoric triamide. After drying, the fabric was exposed to temperatures in the range of 288° C.–316° C. for a period of nine minutes. At this stage of carbonization the fabric had a carbon content of 60.8%. Other combinations of time and temperature produced the same result. The fabric was then passed through a zone heated to 1200° C. for a period of approximately 20 seconds. During this time the carbon level increased to 88%. The carbonized fabric was flexible and exhibited a high tensile strength in both warp and filling directions.

(N) The same fabric was impregnated with a 5% by weight solution of phosphoric triamide and exposed to a heating cycle consisting of a gradual increasing temperature from 230° C. over a period of fifteen minutes. The fabric was then exposed to a temperature of 1538° C. for a period of 20 seconds. The resultant carbonized fabric had a carbon content of 95%. The fabric had excellent tensile strength and was flexible and uniformly lustrous.

(O) Comparable results were obtained on the same fabric treated with 5% by weight aqueous solutions of the following catalysts: phosphorothioic triamide, (chloromethyl)phosphonothionic diamide, phosphonitrile amide cyclic trimer, trimethyl phosphate, triethyl phosphate, diethyl methylphosphoramidate, diethyl ethylphosphoramidate, diethyl isopropylphosphoramidate, and methylphosphonic diamide.

Since the disclosure in U.S. 3,294,489 (Millington) states that flameproofing agents generally, particularly phosphates, borates, and chlorides would be effective catalysts, several known flameproofing agents were evaluated and were not found to be effective catalysts. For example, a boric acid-metaborate mixture, even at the 5% concentration level did not give a satisfactory product at carbonization temperatures of 260° C., 275° C., 288° C. at ten minutes' residence time followed by the usual twenty seconds at 1372° C. Similarly, a borax-boric acid mixture at 5 and 10% concentration at 288° C. for periods of six and nine minutes followed by exposure at the usual 1372° C. for twenty seconds did not give a product of over 82% carbon and the product was too brittle for testing. The above data confirmed that the choice of catalyst even from the class of flame retardants is an empirical selection and successful catalysts cannot be predicted in advance.

As the above data indicate, the novel catalysts of this invention are advantageous in several respects. In some instances they offer advantages over prior-art catalysts exemplified by diammonium hydrogen phosphate. For example, all the catalysts can be applied at room temperature and most of the catalysts function well even at much shorter residence times in the initial carbonization. The lower temperature application is more convenient and reduces safety hazards while the lower residence times effect substantial savings in labor and product costs. The preferred compositions such as phosphoric triamide, phosphorothioic triamide, phosphonitrile amide cyclic trimer, diethyl ethylphosphoramidate, and diethyl methylphosphoramidates not only reduce residence time considerably but actually yield a product having superior physical properties.

As the various examples and discussion in the specification have previously indicated, numerous changes and modification of reagents and reaction conditions can be made without departing from the inventive concept. The metes and bounds of the invention are best described by the claims which follow.

What is claimed is:

1. A process for improving the thermal carbonization of cellulosic fibrous substrates comprising treating said substrates prior to carbonization with at least a catalytic amount of a catalyst of the formula

wherein G is selected from the group consisting of —OR and

R is an alkyl radical having from 1 to 4 carbon atoms; R' and R^2 are selected from the group consisting of hydrogen and R; L is selected from the group consisting of alkyl radicals containing from 1 to 4 carbon atoms, halogenated alkyl radicals containing from 1 to 4 carbon atoms and G; and Z is selected from the group consisting of oxygen and sulfur, and heating said treated substrates until a carbonized product having a carbon content of at least 50% by weight carbon is produced.

2. The process of claim 1 wherein the treated substrate is heated until a carbonized product having a carbon content of at least 80% by weight carbon is produced.

3. A process for improving the thermal carbonization of cellulosic fibrous substrates comprising treating said substrates prior to carbonization with at least a catalytic amount of catalyst selected from the group consisting of phosphorothioic triamide, phosphoric triamide, N,N',N''-trimethylphosphoric triamide, (chloromethyl)phosphonothionic diamide, trimethyl phosphate, triethyl phosphate, diethyl methylphosphoramidate, diethyl ethylphosphoramidate, diethyl isopropylphosphoramidate, methylphosphonic diamide, and mixtures thereof, and heating said treated substrates above 260° C. until a carbonized product having at least 80% by weight of carbon is produced.

4. The process of claim 3 wherein the cellulosic substrate is rayon and the catalyst is applied in the form of an aqueous solution.

5. The process of claim 4 wherein the catalyst is phosphorothioic triamide.

6. The process of claim 4 wherein the catalyst is phosphoric triamide.

7. The process of claim 4 wherein the catalyst is N,N', N''-trimethylphosphoric triamide.

8. The process of claim 4 wherein the catalyst is (chloromethyl)phosphonothionic diamide.

9. The process of claim 4 wherein the catalyst is trimethyl phosphate.

10. The process of claim 4 wherein the catalyst is triethyl phosphate.

11. The process of claim 4 wherein the catalyst is diethyl methylphosphoramidate.

12. The process of claim 4 wherein the catalyst is diethyl ethylphosphoramidate.

13. The process of claim 4 wherein the catalyst is diethyl isopropylphosphoramidate.

14. The process of claim 4 wherein the catalyst is methylphosphonic diamide.

15. The process of claim 4 wherein the substrate is treated with a mixture of the catalysts.

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EDWARD J. MEROS, Primary Examiner

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8—116, 116.2; 23—209.1; 117—136, 138