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C6AX C6X L4C L6D



(54) FLAME RETARDING LINEAR POLYESTERS AND PROCESS FOR THEIR PREPARATION

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flame retarding synthetic linear polyesters which contain units of carboxy-phosphinic acids.

Shaped articles, such as filaments and fibers, of linear polyesters which contain in the polymer molecule phosphorus-containing compounds, for example, various acids of phosphorus and their derivatives for example, phosphonic acids and phosphinic acids, are known. German Auslegeschrift No. 1,243,819 describes filaments and fibers obtained from polyesters modified with phosphonic acid esters; the filaments and fibers are well suited for dyeing with basic and disperse dyestuffs, and they have a low pilling tendency.

According to German Offenlegungsschrift No. 1,520,079 and German Offenlegungsschrift No. 1,595,598, phosphonic and phosphinic acids or their esters are added in the course of the processes for the preparation of fiber-forming linear polyesters, and incorporated into the polymer chains. The main purpose of this modification is to improve the dyeing properties of the filaments and fibers, and this is the only purpose of the modification of polyesters with bis-(*p*-carboxyphenyl)-phosphinic acid as described in German Auslegeschrift No. 1,232,348.

However, it is also known that polyesters comprising phosphorus-containing compounds may have flame-resistant properties. Thus, French Patent No. 1,196,971 disclosed copolyesters containing phosphonic acid units which are resistant to flames and heat. These copolyester products can be used as flame-protection agents, adhesives, varnishes and impregnating substances for paper and textiles as well as intermediate products. On the other hand, it is not possible to spin these polyesters to yield filaments or fibers, since their phosphorus content imparts brittleness to the products.

It has been suggested that flame-resistant polyesters can be prepared by incorporating by condensation into the polyester molecules, alkylene-diphosphinic acids, arylene-di-phosphinic acids or aralkylene-di-phosphinic acids which may also contain additional atoms such as F, Cl, Br, O and S; these polyesters can be worked up to filaments, fibers and to shaped articles (German Offenlegungsschrift Nos. 2,236,037; 2,328,343; 2,236,038 and 2,236,039). However, due to their occasionally rather considerable volatility at the condensation temperatures, it is quite difficult to incorporate the diphosphinic acids by condensation. Therefore, quite frequent use is made of non-volatile oligomers of diphosphinic acids with diols which can be incorporated by condensation; this means, however, that these oligomers have to be prepared first.

Another method for preparing flame-resistant polyesters has also been carried out in such a way that phosphorus compounds which are not built into the polymer chains were incorporated into the polyesters. As such additives there have been used—according to the Japanese Patent Publications Nos. 7,142,230 and 7,142,231—certain esters of phosphoric acid of halogen-containing aromatic dihydroxy-compounds—and according to Belgian Patent No. 769,229—particular polyphosphonates and poly-

(phosphonate-phosphates). Although the use of these additives leads to good, but im-

permanent flame-protection properties, some disadvantages also occur. These disadvantages are mainly a consequence of the considerable migratory properties of the additives in the polymers, leading first to a certain toxicity of the polymer products, and also to the fact that these additives can be washed out relatively easily, for example in the course of dry cleaning of articles made from the corresponding fibers. When the additives are washed out of the articles, the polymer products lose their flame-resistant properties.

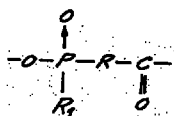
While preparing such fibers, the additives are often responsible for adhesion of the polymer chips during the drying process, as a consequence of the additives tending to migrate to the surface of the polymer chips. The polymer additives described by Belgian Patent No. 769,229 have such a high viscosity that mixing them homogeneously with the polyesters is rather difficult, and they cause undesirably high diglycol contents when the additives are blended in while the polyester-forming reaction is still proceeding.

A comparison with polymers in which the phosphorus compounds have been incorporated into the polymer chain shows that the polymers with additives have poorer dyeing properties. Even red phosphorus has already been used as an additive for producing flame-repellent and self-extinguishing properties of polyester fibers and filaments (German Offenlegungsschrift No. 2,148,348).

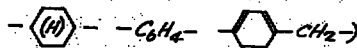
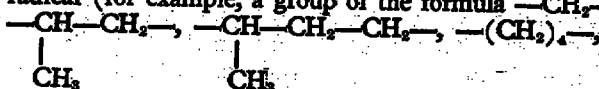
Even though such filaments and fibers are then sufficiently flame-resistant or self-extinguishing, the addition of red phosphorus does not permit the preparation of white products—thus the products obtained are of limited use only.

The present invention seeks to produce permanently flame-retarding linear polyesters, the filaments and fibers thereof having textile properties which compare favorably with filaments and fibers made of the corresponding non-modified polyesters, and which can be processed to yield sheets and other shaped articles. In addition, there was sought a modification agent which is not volatile during the process of incorporation by condensation.

Accordingly, the present invention provides a linear polyester comprising units derived from a dicarboxylic acid and units derived from a diol and from 3 to 20 mol %, based on the total acid-derived units, of phosphorus-containing units of the formula



in which R represents a saturated cyclic or acyclic alkylene radical preferably having from 1 to 15, more preferably from 2 to 10 carbon atoms or an arylene or aralkylene radical (for example, a group of the formula $-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$, $-(\text{CH}_2)_n-$, $-\text{CH}(\text{CH}_3)-\text{CH}_2-$, $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-$, $-(\text{CH}_2)_4-$,

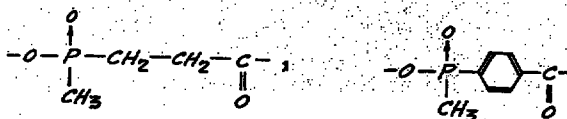


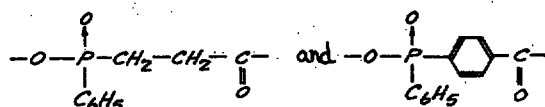
and R_1 represents an alkyl radical having up to 6 carbon atoms, an aryl radical or an aralkyl radical (for example, a radical of the formula CH_3 , C_2H_5 , n - and i - C_4H_9 , C_6H_{11} , C_6H_{13} , C_6H_5 , $\text{C}_6\text{H}_5-\text{CH}_2$), and one or both of R and R_1 may be substituted by a fluorine, chlorine or bromine atom or a sulfonate group and/or may contain an oxygen, sulfur or nitrogen heteroatom.

Preferred phosphorus-containing units are those of the above general formula in which

R is $-\text{CH}_2-\text{CH}_2-$ or C_6H_4 and

R_1 is CH_3 or C_6H_5 , that is to say,

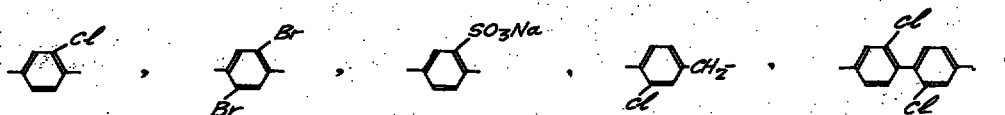




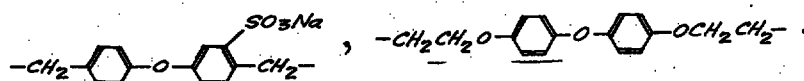
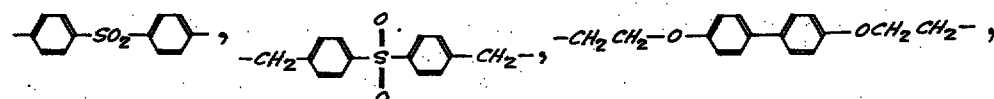
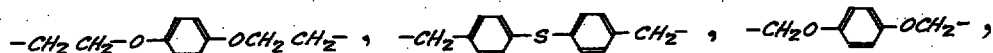
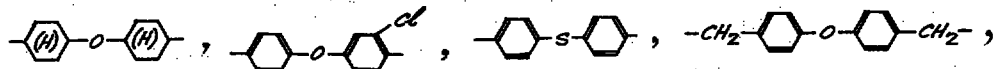
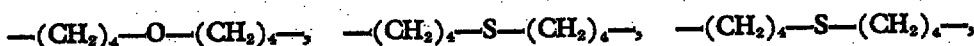
The radicals R and R₁ may be substituted by halogen (F, Cl, Br) atoms or sulfonate groups, and/or may contain oxygen, sulfur or nitrogen heteroatoms; most suitable in this latter respect are O atoms and S atoms. Although N atoms are possible chain members as —NH— or substituted —NH—, they are less appropriate, since N-compounds are often responsible for undesirable discoloration during the polycondensation.

The sulfur heteroatoms can be present as sulfide groups, sulfoxide groups or sulfone groups.

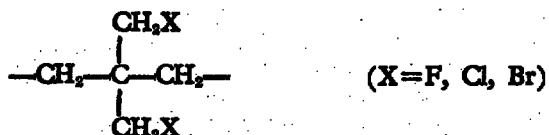
The following are examples of radicals R containing substituents or heteroatoms:



and



When R is a saturated, acyclic or cyclic alkylene radical, it can be halogen-substituted only, provided that the compounds do not or only slightly separate hydrogen halide during preparation of the polyester. Suitable halogen-substituted alkylene-radicals are, for example, those of the formula

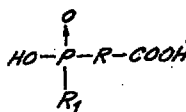


and perfluorinated alkylene radicals.

The radical R₁ may also contain substituents and/or heteroatoms in a similar manner; the most suitable substituents, however, are halogen atoms and the sulfonate group, for example, the following



The present invention also provides a process for preparing the linear polyesters described above, which comprises reacting one or more dicarboxylic acids or their esters with aliphatic alcohols having from 1 to 4 carbon atoms, preferably terephthalic acid or dimethylterephthalate, with one or more diols, preferably ethylene glycol, and with from 3 to 20 mol %, based on the total acid components, of a compound of the formula



in which R and R₁ have the meanings given above, or an ester thereof with an aliphatic alcohol having from 1 to 4 carbon atoms, or a diol which is the diol component of the polyester, or a cyclic anhydride thereof.

In this process, the usual starting materials which are known to be most suitable for preparing high-molecular weight and particularly fiber-forming and film-forming linear polyesters are reacted in known manner, and prior to, during or shortly before the end of the polycondensation, there are added bifunctional carboxy-phosphinic acids or their esters with alcohols having from 1 to 4 carbon atoms, or with a diol, which forms the diol component of the polyester. It is also possible to use the oligomers of the carboxy-phosphinic acid-diol esters. It is also possible to use the cyclic anhydrides of phosphinic-carboxylic acids which form easily and are readily prepared. The quantity of the carboxy-phosphinic acid-component is from 3 to 20 mol.% of the total acid component, i.e. dicarboxylic acid(s) and carboxy-phosphinic acid(s).

The preferred dicarboxylic acid is terephthalic acid, and other dicarboxylic acids can be used as co-components. The acid component may be free or esterified with an aliphatic alcohol having from 1 to 4 carbon atoms, especially methanol. Most suitable for use as co-components are for example, isophthalic acid, 5-sulfo-isophthalic acid, 5-sulfopropoxy-isophthalic acid, naphthalene-2,6-dicarboxylic acid, diphenyl-*p*, *p'*-dicarboxylic acid, *p*-phenylene-diacetic acid, diphenyloxide-*p*, *p'*-dicarboxylic acid, diphenoxy-alkane-dicarboxylic acids, trans-hexahydro-terephthalic acid, adipic acid, sebacic acid, and 1,2-cyclo-butane-dicarboxylic acid.

Suitable diol-components are those of the formula HO(CH₂)_nOH in which *n* is an integer from 2 to 10, for example propane-diol-1,3, butane-diol-1,4 and the higher homologues, preferably ethylene glycol, as well as for example 2,2-di-methyl-propanediol-1,3 and, preferably, 1,4-cyclohexane-dimethanol. Co-components for the diol may also be used.

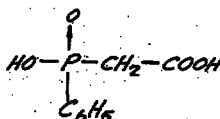
When, besides terephthalic acid, use is made of additional dicarboxylic acids, it is preferable that the latter comprise not more than 10 mol.% of the total acid component used. A similar pattern is followed for the composition of the diol component. For example, if further diols—besides the ethylene-glycol, are used, their quantity preferably does not exceed 10 mol.% of the total diol component.

If the starting materials are free dicarboxylic acids and diols, the first step of the process is esterification, followed by polycondensation. If the starting materials are dicarboxylic acid esters—especially dimethyl esters—the first step is transesterification and then polycondensation, each of these steps being carried out in the presence of the usual catalysts.

The usual additives (for example, cross-linking agents, delusterants and stabilizers, nucleating agents, coloring agent and fillers) can be added during the preparation of the polyesters, in addition to the usual catalysts.

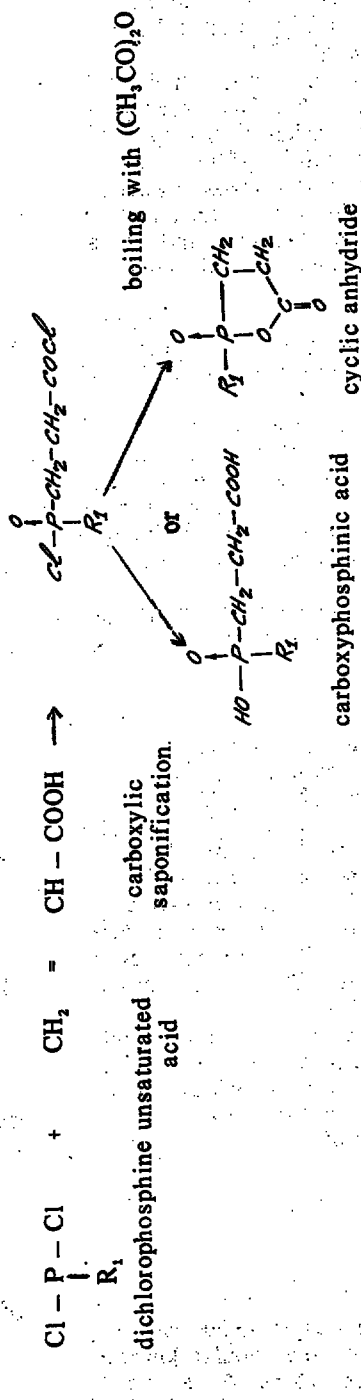
The bifunctional carboxyphosphinic acids which are added prior to, during or shortly before termination of the polycondensation, or their esters or their cyclic anhydrides can be prepared as follows:

Carboxyphosphinic acid having only one carbon atom between the P-atom and the COOH-group are obtained, for example, according to the reaction described by H. G. Hennig and G. Hilgetag in "J. Prakt. Chem. 29, 86 ff (1965), starting from α-Cl or α-Br-acetic acid alkyl esters and phosphonous acid alkyl esters. A carboxymethyl-phenyl-phosphinic acid having for example, the formula



is obtainable by this method.

When R is an alkylene group having 2 or more carbon atoms, it is useful to follow approximately the reaction scheme described by V. K. Chajrullin et al in Z. Obsc. Chim. 37 (1967) No. 3, pg. 710—714, starting from dichlorophosphines and unsaturated carboxylic acids, for example:—



$\text{R}_1 = -\text{CH}_3$

$-\text{C}_2\text{H}_5$

$-\text{C}_6\text{H}_5$

$-\text{C}_6\text{H}_4 - \text{CH}_3$

Among the unsaturated acids preference is given to the use of acrylic acid, methacrylic acid and crotonic acid.

Carboxyphosphinic acids having an aromatic radical ($\text{R} = \text{arylene}$) between the P atom and the COOH -group can be prepared for example, according to the process described by L.D. Quin et al in J. Org. Chem. 27, 4120 (1962) or according to the process described in our copending Application No. 40287/74 (Serial No. 1,469,350) filed concurrently herewith.

The latter process involves reacting halobenzoic acid esters with phosphonous acid diesters in an Arbuzov reaction. The carboxyalkyl-phosphinic acid esters can be hydrolysed or saponified for example with strong inorganic acids or bases.

Carboxyphosphinic acids in which R is an aralkylene group can be prepared in analogy to the method described in Belgian Patent No. 601,710 from carboxybenzylhalides and phosphonous acid esters and subsequent saponification of the esters groups to yield free acids.

The carboxyphosphinic acids and their esters and cyclic anhydrides are not volatile under the conditions of the polyester-forming reaction—in contrast to, for example various diposphinic acids—so that the former may be completely incorporated by condensation.

The phosphorous-organic structural unit is then randomly distributed in the macromolecule of the polyester product. Occasionally the carboxyphosphinic acid units may also be present as terminal groups, due to their random distribution. So as to

guarantee the desired flame-resistant properties, moulding compositions should preferably include at least 0.5 wt.% of phosphorus in the polyester, whilst the amount present in filaments and fibers should preferably amount to at least 1 wt.%. The flame-retarding qualities are further improved if the P-containing chain members in the polyesters include halides as substituents.

Subsequently, the completely condensed polyesters are spun to filaments and fibers in the usual manner, stretched and submitted to additional treatment or extruded to yield sheets or worked-up to obtain shaped articles by press-moulding, injection-moulding or extrusion. Especially suitable are filaments, fibers, sheets and shaped articles, the dicarboxylic acid component of which contains mainly terephthalic acid and the diol component of which comprises essentially ethylene-glycol.

The fibers and filaments have very good and permanent flame-resistant or self-extinguishing properties. Having a good degree of whiteness, they have very good dyeing properties for disperse dyestuffs and their receptivity includes acid dyestuffs in colour shades of average to deep intensity. When the P-containing chain members additionally include sulfonate groups, the receptivity also extends to basic dyestuffs. The amount of diglycol units in the polyesters is only slightly greater than that of corresponding unmodified polyesters; the tensile strength of the filaments and fibers, second order transition temperature and melting point, correspond approximately to the values of corresponding unmodified polyesters.

Such fibers and filaments find many applications where rapidly ignitable textiles and technical articles cannot be admitted, for example for awning cloths, carpets, and curtains. It is also possible to use such filaments as one of the components in bi-component-filaments in combination with other polymers.

The sheets and shaped articles can be used wherever intense risks of ignition and fire exist. If the transparency of the shaped articles is of no concern, their solidity can be enhanced by imbedding, for example inorganic fiber materials such as glass fibers, fibers of quartz, asbestos and carbon in the usual quantities. As examples of such shaped articles there can be mentioned casings, constructional parts, electric machinery, mechanical transmission parts, hollow articles, particle units in large-scale computers and sensitive electronic apparatus.

The following Examples illustrate the invention: the percentages are by weight unless otherwise indicated. The mol% values given for the carboxyphosphinic acids are based on the total acid components in each case.

EXAMPLE 1.

1,000 g of dimethyl terephthalate are transesterified with 720 ml of ethylene glycol in the presence of 230 mg of manganese acetate, 4 H₂O as catalysts, the transesterification taking place under nitrogen at temperatures of from 170 to 220° C. After completion of the separation of methanol, 100 g. (11.3 mol%) of 2-carboxy-ethyl-methylphosphinic acid (preparation according to V. K. Chajrullin et al, Z. obsch. Chim. 37 (1967) No. 3, pg. 710—714) are added at 220° C and esterified.

After having added 350 mg of Sb₂O₃, the reaction vessel is further heated and, simultaneously, evacuated slowly to a pressure of 1 torr at 250° C. Polycondensation is carried out at 0.2 torr and at 275° C until a relative viscosity (measured as a 1% solution in dichloroacetic acid at 25°) of 1.85 is attained. The product has a melting point of 244 to 248° C, and a phosphorus content of 1.85%.

The condensation product was spun from the melt under the usual conditions and, subsequently, stretched in a proportion of 1:3.65. The threads obtained showed a resistance of 33 g/tex at an elongation at break of 35%. They were worked up to a tubular knitted article which was used for dyeing and flammability tests.

Dyeing with the acid dyestuffs having the commercial names of

"Supranol Echartrot" (C.I. no. 24 790) (Red)

"Alphanol Echartblau FGLL" (C.I. no. 62155) and (Blue)

"Lanaperigelb 3 G" (C.I. no. 19 025) (Yellow)

yielded deep colour shades.

The flammability test was carried out according to the oxygen-index method as per the test regulation ASTM 2863—70. For that purpose the tubular knitted article was fitted vertically into the apparatus and ignited from above. An artificial oxygen/nitrogen atmosphere was created with a given oxygen content barely allowing for the test knit to burn.

A value of 29 vol.% of O₂ was found. A corresponding tubular knitted article

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made of unmodified polyethylene-terephthalate started burning in a N_2/O_2 mixture having an oxygen content of 20 vol.%.
[unclear]

EXAMPLES 2—8.

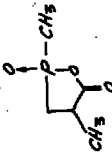
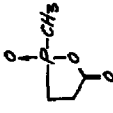
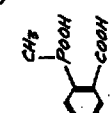
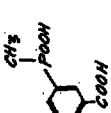
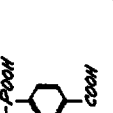
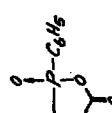
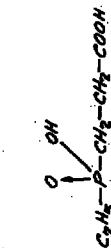
The test described in Example 1 was repeated with different carboxyphosphinic acids or their derivatives incorporated into polyester molecules. The following table shows the results.

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TABLE

Examples 2 - 8

Example No.	Modification agent	Preparation according to:	quantity added g.	rel. (†) viscosity	melting point °C	P- content wt. %	Oxygen index value vol. %
2		V.K. Chajrullin et al. Z.obsc.Chim. 38 (1968) Nr. 2. S. 288-292	100 (11.6 mol%)	1.75	240-242	1.9	30
3		V.K. Chajrullin et al. Z.obsc.Chim. 37 (1967) Nr. 3. S. 710-714	80 (10.4 mol%)	1.89	241-245	1.6	30
4			90 (8.0 mol%)	1.54	243-245	1.25	28
5		Appl. No. 40287/74 (Serial No. 1469350).	100 (8.85 mol%)	1.87	241-243	1.4	29
6			100 (8.85 mol%)	1.81	247-249	1.4	29
7		V.K. Chajrullin et al. Z.obsc. Chim. 37 (1967) Nr. 2. S. 155-160	125 (11.0 mol%)	1.79	240-244	1.7	30
8		V.K. Chajrullin et al. Doklady Akad. SSSR 162 (1965) Nr. 4. S. 827-828 or Z.obsc. Chim. 42 (1972) Nr. 8 S. 1730-1733	75 (8.05 mol%)	1.77	245-247	1.3	27.5

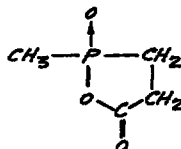
(†) measured as described in Example 1.

EXAMPLE 9.

Example 1 was repeated, but 6 mol.% of dimethyl terephthalate was replaced by dimethyl-isophthalate for the transesterification. The polymer melting point was 236—238° C. The relative viscosity was 1.82. Tubular knitted articles made of this material have an oxygen index value of 30%.

EXAMPLE 10.

Example 1 was repeated with the difference that, instead of 100 g of 2-carboxy-ethyl-methyl-phosphinic acid, there were used 75 g (9.8 mol%) of its cyclic anhydride 2-methyl-2,5-dioxo-1-oxa-2-phospholane having the formula



and, instead of 350 mg of Sb_2O_3 , 300 mg of GeHPO_4 .

The pure white polyester containing 1.5% of phosphorus was crushed cold. The reduced specific viscosity of the granules was 1.08 (measured in phenol/tetrachloroethane=3:2 at 25° C). The viscosity of the granules was improved to 1.36 by solid condensation in a rotating vessel at 230° C and at 0.2 torr, for a period of 8 hours.

The granules were worked up to plates on an injection moulding machine, the cylinder having temperatures of 260°/270°/260° C, the moulding temperature being 20° C. The plates measuring 60 × 60 × 2 mm were transparent and completely colourless, their reduced specific viscosity was 1.25. The impact strength of the plates was examined by means of the drop hammer test, exposing the plates to the vertical impact of a dropping object (drop hammer) from various heights, the plates clamped onto a frame. The tip of the drop hammer was a hemisphere of radius 10 mm, and the hammer had a weight of 1 kg. For each height 10 plates were submitted to the test. At a given dropping height of 150 cm the impact was strong enough to crush 50% of the plates. The impact strength of the plates of the Example was 200 cm.

Plates obtained under the same conditions but without the phosphorous modification compound having a reduced specific viscosity of 1.32 had an impact strength of 190 cm when submitted to impact under the same conditions.

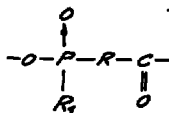
For the flammability test the granules were pressed to plates 1.3 mm thick at a temperatures between 230 and 250° C and under a pressure of 80 atm. From these plates were cut test specimens measuring 127 × 12.7 mm. The result of the flammability test according to ASTM D 635—68 was "non-ignitable", the flammability test being carried out according to Underwrites Laboratories (UL) Subject 94 "SE O".

EXAMPLE 11.

Example 10 was repeated with the difference that instead of 75 g of 2-methyl-2,5-dioxo-1-oxa-2-phospholane only 35 g (4.8 mol%) of this compound were used. The phosphorus content was then 0.7%. The flammability test according to ASTM D 635—68 showed as result "self-extinguishing".

WHAT WE CLAIM IS:—

1. A linear polyester comprising units derived from a dicarboxylic acid and units derived from a diol and from 3 to 20 mol%, based on the total acid-derived units, of phosphorus-containing units of the formula



in which R represents a saturated, cyclic or acyclic alkylene radical, an arylene radical or an aralkylene radical and R_1 represents an alkyl group having up to 6 carbon atoms, an aryl group or an aralkyl group, and one or both of R and R_1 may be substituted by a fluorine, chlorine or bromine atom or a sulfonate group and/or may contain an oxygen, sulfur or nitrogen heteroatom.

2. A linear polyester according to claim 1, wherein the saturated cyclic or



* C L M S *

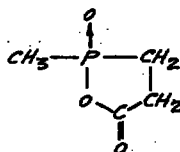
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EXAMPLE 10.

Example 1 was repeated with the difference that, instead of 100 g of 2-carboxy-ethyl-methyl-phosphinic acid, there were used 75 g (9.8 mol%) of its cyclic anhydride 2-methyl-2,5-dioxo-1-oxa-2-phospholane having the formula



and, instead of 350 mg of Sb_2O_3 , 300 mg of GeHPO_3 .

The pure white polyester containing 1.5% of phosphorus was crushed cold. The reduced specific viscosity of the granules was 1.08 (measured in phenol/tetrachloroethane=3:2 at 25° C). The viscosity of the granules was improved to 1.36 by solid condensation in a rotating vessel at 230° C and at 0.2 torr, for a period of 8 hours.

The granules were worked up to plates on an injection moulding machine, the cylinder having temperatures of 260°/270°/260° C, the moulding temperature being 20° C. The plates measuring 60 × 60 × 2 mm were transparent and completely colourless, their reduced specific viscosity was 1.25. The impact strength of the plates was examined by means of the drop hammer test, exposing the plates to the vertical impact of a dropping object (drop hammer) from various heights, the plates clamped onto a frame. The tip of the drop hammer was a hemisphere of radius 10 mm, and the hammer had a weight of 1 kg. For each height 10 plates were submitted to the test. At a given dropping height of 150 cm the impact was strong enough to crush 50% of the plates. The impact strength of the plates of the Example was 200 cm.

Plates obtained under the same conditions but without the phosphorous modification compound having a reduced specific viscosity of 1.32 had an impact strength of 190 cm when submitted to impact under the same conditions.

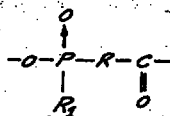
For the flammability test the granules were pressed to plates 1.3 mm thick at a temperatures between 230 and 250° C and under a pressure of 80 atm. From these plates were cut test specimens measuring 127 × 12.7 mm. The result of the flammability test according to ASTM D 635—68 was "non-ignitable", the flammability test being carried out according to Underwrites Laboratories (UL) Subject 94 "SE O".

EXAMPLE 11.

Example 10 was repeated with the difference that instead of 75 g of 2-methyl-2,5-dioxo-1-oxa-2-phospholane only 35 g (4.8 mol%) of this compound were used. The phosphorus content was then 0.7%. The flammability test according to ASTM D 635—68 showed as result "self-extinguishing".

WHAT WE CLAIM IS:—

1. A linear polyester comprising units derived from a dicarboxylic acid and units derived from a diol and from 3 to 20 mol%, based on the total acid-derived units, of phosphorus-containing units of the formula



in which R represents a saturated, cyclic or acyclic alkylene radical, an arylene radical or an aralkylene radical and R_1 represents an alkyl group having up to 6 carbon atoms, an aryl group or an aralkyl group, and one or both of R and R_1 may be substituted by a fluorine, chlorine or bromine atom or a sulfonate group and/or may contain an oxygen, sulfur or nitrogen heteroatom.

2. A linear polyester according to claim 1, wherein the saturated cyclic or

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acyclic alkylene radical has from 1 to 15 carbon atoms.

3. A linear polyester according to claim 1, in which

R is $-\text{CH}_2-\text{CH}_2-$ or $-\text{C}_6\text{H}_4-$ and

R₁ is CH_3 or C_6H_5 .

4. A linear polyester according to any one of claims 1 to 3, wherein the hetero atoms are O or S atoms.

5. A linear polyester according to any one of claims 1 to 4, wherein the dicarboxylic acid-derived units consist essentially of units of terephthalic acid, and the diol-derived units consist essentially of units of diols of the formula

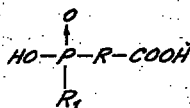


in which n is an integer from 2 to 10, or of units of 1,4-cyclohexane-dimethanol.

6. A linear polyester according to any one of claims 1 to 5, wherein the dicarboxylic acid-derived units consist essentially of units of terephthalic acid and the diol-derived units consist essentially of units of ethylene glycol.

7. A linear polyester according to claim 1 substantially as described in any one of Examples 1 to 11 herein.

8. A process for preparing a linear polyester according to claim 1, which comprises reacting one or more dicarboxylic acids or their esters with aliphatic alcohols having from 1 to 4 carbon atoms, preferably terephthalic acid or dimethylterephthalate, with one or more diols, preferably ethylene-glycol, and with from 3 to 20 mol.%, based on the total acid components, of a compound of the formula



in which R and R₁ have the meanings specified in any one of claims 1 to 4, or with an ester thereof with an aliphatic alcohol having from 1 to 4 carbon atoms or a diol which is the diol component of the polyester or with a cyclic anhydride thereof.

9. A process according to claim 8 carried out substantially as described in any one of Examples 1 to 11 herein.

10. A linear polyester whenever prepared by a process according to claim 8 or claim 9.

11. A shaped article comprising a linear polyester according to any one of claims 1 to 7.

12. A shaped article according to claim 11 in the form of a filament, fiber or sheet.

13. A shaped article according to claim 11 or claim 12 which has been prepared by press-moulding, injection moulding or extrusion.

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