(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 August 2003 (28.08.2003)

(10) International Publication Number
WO 03/070773 A1

(51) International Patent Classification:
C08B 31/04, 33/02, 35/02, D06M 15/11

(21) International Application Number:
PCT/US03/04083

(22) International Filing Date:
12 February 2003 (12.02.2003)

(25) Filing Language:
English

(26) Publication Language:
English

(30) Priority Data:
60/357,503 15 February 2002 (15.02.2002) US

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Published: with international search report
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: NOVEL REACTION PRODUCT OF STARCHES AND AROMATIC ACIDS AND/OR AROMATIC ANHYDRIDES

(57) Abstract: This invention relates to the reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein the starch is reacted in the solid state with solid state reactants comprising the aromatic anhydride and/or aromatic acid, and at a time and temperature sufficient to obtain a reaction between the anhydride and/or acid.
NOVEL REACTION PRODUCT OF STARCHES AND AROMATIC ACIDS
AND/OR AROMATIC ANHYDRIDES

FIELD OF THE INVENTION

The field of the invention relates to the reaction of at least one starch
with at least one aromatic anhydride and/or an aromatic acid.

BACKGROUND OF THE INVENTION

Starch based polymers have been known to be desirable for the
development of food products, fibers, filaments, plastics, and other
products.

United States Patent 4,212,704 (Durand et al.) discloses the reaction
of starches with dibasic anhydrides (aromatic or aliphatic) in warm aqueous
slurries prior to blending with clays, fibers, and possibly other materials in
the manufacture of fiberboard. Durand et al. does not teach the reaction of
starches with anhydrides in the dry or solid state. It also teaches the
reaction of starches with anhydrides in the presence of a base catalyst.

United States Patent 2,461,139 teaches the treatment of starch, in
the presence of water, with organic acid anhydrides. This patent also
discloses that, previously, it had been considered impossible to react
starch, in the presence of water, with organic acid anhydrides but that an alkaline medium is essential.

      Reactions of starches with aromatic anhydrides are generally known in the art. However, the reactions known in the art require either a slurry of starch in water, an organic solvent or a base catalyst.

      Many types of textile warp sizes have been used in the past. In particular, starch, starch derivatives, and animal glue have been used in the case of cotton yarns, whereas polyvinyl alcohol has found wide acceptance as a size for yarns of synthetic materials, most commonly cellulose acetate and polyesters, such as polyethylene terephthalate, and blends of polyester fibers with cotton or rayon.

      It is well known in the art that neither unmodified starches nor starches modified by acid hydrolysis, oxidation, ethoxylation, propoxylation, acylation with acetic anhydride, carboxymethylation or phosphation are suitable alone or in conjunction with non-film forming auxiliaries for sizing spun textile yarns containing polyester. Typically the size formulation will contain either fully or partially hydrolyzed polyvinyl alcohol. This compound will normally comprise anywhere from 30-60% of the total solids in a size formula. The remainder of the size mix being an unmodified or modified starch as previously described, binder (such as sodium polyacrylate,) humectant, and lubricant (normally hydrogenated tallow glycerides.)

      Polyvinyl alcohol is relatively expensive as compared to starch products, being as much as 5 times the cost of unmodified corn starch. It is generally understood that starch and the commercial modifications previously described do not adhere to polyester containing yarns well enough to process the yarn into fabric without an impractical number of broken warp ends.

      In view of the foregoing, it would be an advancement in the art to provide a novel and economical textile sizing agent with improved adhesion
to films, and to fibers and yarns, preferably to polyester fibers and films and polyester containing fibers, yarns and films. Specifically, it is the modification of such starches by acylation with aromatic anhydrides and/or aromatic acids that assists in improving these adhesion properties.

Moreover, it is the purpose to this invention to replace part or all of the polyvinyl alcohol used to size such yarns, thereby providing improved economics to the sizing process.

SUMMARY OF THE INVENTION

In one aspect of this invention, there is provided a reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein the starch is reacted in the solid state with solid state reactants comprising the aromatic anhydride and/or aromatic acid, in the absence of a base catalyst, at a time and temperature sufficient to obtain a reaction between the aromatic anhydride and/or acid and the starch(es) to form an ester substituent group.

In a second aspect of the invention, there is provided a reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein the starch is reacted in the solid state with solid state reactants comprising the aromatic anhydride and/or aromatic acid, and at a time and temperature sufficient to obtain a reaction between the aromatic anhydride and/or acid and the starch(es) to form an ester substituent group; and wherein, during the solid state reaction, the solid state reactants have a total water content of 0 to 6.0 weight % based on a total weight percentage for the solid state reactants of 100 weight %. In this embodiment, the presence of a base catalyst is not necessary.

In a third aspect of the invention, a textile sizing agent comprising the reaction products described above is provided. The textile sizing agents of the invention are preferably applied to yarns containing polyester fibers.
In a fourth aspect of the invention, a textile agent sized with the reaction products of the invention is provided.

In a fifth aspect of the invention, a process for sizing a textile substrate material comprising applying to the textile material a composition comprising the reaction products of the invention is provided.

In a sixth aspect of the invention, a process for making a modified starch is provided comprising the step of reacting solid state reactants comprising at least one aromatic anhydride and/or aromatic acid with one or more starches in the solid state at a time and temperature sufficient to obtain a reaction between the aromatic anhydride and/or acid and the starch(es) to form an ester substituent group; and wherein, during the solid state reaction, the solid state reactants have a total water content of 0 to 6.0 weight % based on the total weight percentage of the solid state reactants equaling 100 weight %. In this embodiment, the presence of a base catalyst is not necessary.

The present invention provides improved adhesion properties when applied as a textile sizing agent to fibers and/or yarn, preferably polyester fibers and/or yarn either used alone or in combination with other types of fibers. The present invention also provides improved adhesion properties when applied to polyester film.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates primarily to the reaction product of at least one starch in the solid state with solid state reactants comprising at least one aromatic anhydride and/or aromatic acid. The starch is reacted in the solid state with the aromatic anhydride and/or aromatic acid or optionally, with other solid state reactants, at a time and temperature sufficient to obtain a reaction between the anhydride and/or acid and the starch(es) to form an ester substituent group. It is preferred that the reaction proceeds without a
base catalyst. It is also preferred that the reaction occur in the solid state. By "solid state", it is meant that, during the reaction, the solid state reactants have a total water content of 0.0 to 6.0% by weight, preferably less than 5.0% by weight, more preferably 0.1 to 4.0% by weight, and even more preferably, less than 1.0% by weight, wherein the total weight of the solid state reactants equals 100% by weight. By "total water content", it is meant the sum of the water content of all of the solid state reactants present. This may be achieved by drying the reactants either separately or together prior the solid state reaction. The time required to heat the reactor vessel and the reactants to the solid state reaction temperature is not considered herein as part of the solid state reaction time. It is preferred that no water be added during the solid state reaction. The weight % water in the solid state reactants is preferably reduced to less than 0.1% by drying them separately at an elevated temperature prior to the solid state reaction.

It is more preferred that the solid state reactants, preferably, the starch and aromatic anhydride and/or aromatic acid, be dried separately at an elevated temperature under vacuum prior to the solid state reaction. The previously dried solid state reactants (inclusive of the starch and the aromatic acid and/or anhydride) are then preferably mixed and heated at atmospheric pressure for a time and a temperature sufficient to obtain a reaction between the acid and/or anhydride and the starch to form an ester substituent group. It is preferred that the solid state reactants of the invention either consist essentially of or consist of starch and aromatic anhydride and/or aromatic acid and the total water content as defined above for solid state conditions.

The starches useful in the present invention may be any starch known in the art including, but not limited to, one or more starches selected from corn starch, high amylose corn starch, potato starch, sweet potato starch, wheat starch, rice starch, tapioca starch, pea starch, rye starch, oat starch, sago starch and sorghum starch and the amylose and amylopectin
fractions therefrom. It is preferred that the starches be derived from rice, wheat, tapioca, potatoes, and/or corn. Wheat and corn sources are more preferred.

Although not required, it is also preferred that the starch be an acid modified starch and/or that it be in a granulated form. The sizes of the granules are typically from 3-100 microns with reference to the average size of their largest diameter. "Acid modified starch" refers to acid reaction with the starch prior to the reaction of the starch with the aromatic anhydride and/or aromatic acid. In a particular embodiment involving acid modification, the aqueous starch slurry is modified with a suitable acid such as hydrochloric or sulfuric acid at temperatures below the gelatinization point. This occurs prior to the final dewatering operation and after the starch is separated from the gluten and washed. The starch is then treated with 0.1 N acid (sulfuric or hydrochloric acid) at 40-50°C for 6-24 hours, depending on the extent to modification or fluidity desired. The acid hydrolyzes α-1,6 and α-1,4 glucosidic linkages. The reaction is stopped by addition of alkali such as sodium carbonate. The final product is filtered, washed and dried. Examples of acid-modified starches particularly useful in the invention are ANCHOR LR, CLINTON 221, CLINTON 240, and CLINTON 277, which are all commercially available corn starches.

It is preferred that the number average molecular weight of the starch is from 10,000 to 300,000, preferably 80,000 to 120,000. Anhydroglucose units of starch may have either a low or high degree of ester substitution (DS). DS as defined herein as applicable to any feature of the invention is the measure of degree of esterification of the three available hydroxyls of the anhydroglucose units of the starch(es). The maximum DS is three.

The aromatic anhydride and/or aromatic acid of the invention may be any aromatic anhydride known in the art but is preferably selected from trimellitic anhydride, pyromellitic dianhydride (IUPAC name is 1,2,4,5-
benzenetetracarboxylic anhydride), and/or phthalic anhydride. Corresponding acids of the anhydrides may also be used. More preferably, the aromatic anhydride is phthalic anhydride. It is also preferable that the aromatic anhydride and/or aromatic acid is present in the reaction product of the invention in the amount of 0.05 to 6 weight %, preferably, 3.0 – 5.0 weight %, and more preferably, 3.8 to 4.2 weight %, wherein the total weight percentage of starch and aromatic anhydride or aromatic acid equals 100 weight %. It is also preferred that the aromatic anhydride and/or aromatic acid has a particle size of 2 mm or less.

While not being bound by any particular scientific theory, it is believed that the outer surface of the starch granule is reacted with the aromatic anhydride and/or aromatic acid more substantially than the inner portion of said starch granule. As mentioned herein, the language "sufficient to form an ester substituent group" means that the final reaction product has a resultant average degree of substitution (DS) of at least 0.001 DS. The preferred resultant average degree of substitution (DS) of the entire reaction product ranges between 0.001 to 0.10, and more preferably, 0.001 to 0.07 (or stated another way, 0.03 to 2.3 % of the available hydroxyls on the anhydroglucose unit). The average DS of the fraction of material on the outer surface has not been established with certainty, but it could be as high as the theoretical maximum, i.e., 3.0, on some anhydroglucose units.

It is preferred that 2 to 60 g phthalic anhydride, more preferably 10 to 50 g, even more preferably 36 to 42 g phthalic anhydride per 1000 g dry starch is used. While it is within the context of this invention that the reaction occur at any time and temperature sufficient to obtain a reaction between the anhydride or acid and the starch to form an ester substituent group, it is preferred that the reaction time is from 5 to 120 minutes and that the reaction temperature is from 250°F ± 30°F (121°C ± 17°C), preferably, that the reaction time is from 100 to 120 minutes and the reaction
temperature is about 250°F (121°C), and more preferably, that the reaction time is from 20 to 30 minutes and the reaction temperature is from 265°F ± 15°F (129° ± 9°C).

While it is not preferable in one aspect of the invention to have a base present in the solid state reaction of the invention, it is preferred to add a base to the final reaction product to react with the unreacted aromatic anhydride or aromatic acid or carboxylic acid for safety and handling reasons. By "absence of base catalyst or no base catalyst", it is meant that no base is present during the solid state reaction of the invention. Although any base known in the art may be used, it is preferable that the base be selected from the group consisting of ammonia, aqua ammonia, amines, polyamines and amino alcohols. Other known bases can be used as well such as but not limited to potash, potassium hydroxide, soda ash, sodium hydroxide, lithium hydroxide, or trisodium phosphate. The base preferably reacts with any unreacted phthalic anhydride or phthalic acid or carboxylic acid. The addition of base after the solid state reaction is optionally performed due to environmental reasons.

Although the mixing or blending of the starch(es) and the aromatic anhydride and/or aromatic acid may be accomplished by any means known in the art, it is preferred also that the starting materials are mixed in a dry blender during the reaction.

An important embodiment of this invention is the use of the reaction products of the invention as textile sizing agents. Also, an embodiment of the invention is the application of one of the reaction products of the invention to a textile substrate material or textile material. Another embodiment of the invention is textile yarn sized with a textile sizing agent comprising or consisting essentially of one of the reaction products of the invention.

The textile fibers, textile material, textile substrate material of textile yarn (all terms used equivalently) of the invention may be selected from
polyester, cotton, polyacrylcs, polyamides, polyolefins, rayons, and wool. Preferably, it is a polyester or a blend of one or more polyesters with at least one of the following: cotton, polyacrylcs, polyamides, polyolefins, rayons and wool.

The polyesters useful in the invention comprise diacid residues and diol residues. Useful dicarboxylic acids include but are not limited to ones having from 6 to about 40 carbon atoms, and more preferably dicarboxylic acids selected from aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 7 to 12 carbon atoms. Examples of suitable dicarboxylic acids include terephthalic acid, isophthalic acid, 5-sodosulfoisophthalic acid, phthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. The various isomers of naphthalenedicarboxylic acid or mixtures of isomers may be used, but the 1,4-, 1,5-, 2,6-, and 2,7-isomers are preferred. The 1,4-cyclohexanedicarboxylic acid may be in the form of cis, trans, or cis/trans mixtures. In addition, for purposes of this invention, "dicarboxylic acid" includes the lower alkyl ester or acid halide form of the diacid. Further, these ester and acid chloride forms may also be used in place of or in conjunction with the diacid form. Polyesters may be prepared from one or more of the above dicarboxylic acids.

Typical glycols used in the polyester fibers, film and/or yarn of the invention include aliphatic glycols containing from two to about ten carbon atoms, and cycloaliphatic glycols containing 7 to 14 carbon atoms. Preferred glycols include ethylene glycol, propylene glycol, 1, 4-butonediol, 1,6-hexanediol, 1,4-cyclohexanediol, diethylene glycol and the like. The glycol component may optionally be modified with up to about 50 mole %, preferably up to about 25 mole %, and more preferably up to about 15
mole % of one or more different diols. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms, aromatic diols containing from 6 to 15 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include: diethylene glycol, triethylene glycol, trimethylene glycol, 1,4-cyclohexanediolmethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(2-hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, resorcinol, hydroquinone, catechol, bisphenol and its derivatives, and the like. Polyesters may be prepared from one or more of the above diols.

While any polyester may be useful in this invention, a preferred embodiment of the invention relates to a residue of a glycolic component comprising ethylene glycol and polyester comprising a residue of a dicarboxylic acid comprising terephthalic acid. The dicarboxylic acid component of the polyester may optionally be modified with up to about 50 mole% and, optionally, up to about 20 mole % of one or more different carboxylic acids.

In one aspect of the invention, the polyester useful in the fibers, films or yarns of this invention comprises 80 to 100 mole % terephthalic acid residues and 100 to 80 mole % ethylene glycol, more preferably, 90 to 100 mole % terephthalic acid residues and 100 to 90 mole % ethylene glycol, wherein the total mole percentages of the glycol component equal 100 mole % and the total mole percentages of the acid component equal 100 mole %. Poly(ethylene terephthalate) such as that sold in fiber form under the Dacron™ trademark and in film form under the Mylar™ trademark is particularly useful in this invention.
In another aspect of the invention, the polyester useful in the fibers, films or yarns of this invention comprises 80 to 100 mole % terephthalic acid residues and 100 to 80 mole % 1,4-cyclohexanediol residues; more preferably, 90 to 100 mole % terephthalic acid residues and 100 to 90 mole % 1,4-cyclohexanediol residues; wherein the total mole percentages of the glycol component equal 100 mole % and the total mole percentages of the acid component equal 100 mole %.

In yet another aspect of the invention, the polyester useful in the fibers, films or yarns of this invention comprises 80 to 100 mole % terephthalic acid residues, 10 to 50 mole % 1,4-cyclohexanediol, and 90 to 50 mole% ethylene glycol; more preferably, 90 to 100 mole % terephthalic acid residues, 20 to 40 mole % 1,4-cyclohexanediol, and 80 to 60 mole % ethylene glycol; and even more preferably, 90 to 100 mole % terephthalic acid residues, 28 to 35 mole % 1,4-cyclohexanediol residues, and 72 to 65 mole % ethylene glycol residues; wherein the total mole percentages of the glycol component equal 100 mole % and the total mole percentages of the acid component equal 100 mole %.

The polyesters useful in the fibers, films or yarns useful in the present invention are formed via conventional polyesterification and polycondensation techniques. Typical methods for preparing these polyesters are described in United States Patents 2,465,319 and 3,047,539. Any typical additive known in the art may be present in the polyesters of the present invention. However, polyesters useful in this invention may be made by any of several methods known in the art.

The textile sizing agents of the invention comprise the reaction products of the invention. The textile sizing agents of the invention are in turn useful in sizing the textile fibers, textile materials, textile substrates or textile yarns of the invention. When applied to such fibers, materials or
yarn, particularly in the case of polyester fibers blended with other fibers, the textile sizing agent has improved adhesive properties.

The esterified starches, which comprise the reaction products of the invention, may be formulated with any such additives as are known in the art. However, preferred additives include ones commonly incorporated into textiles. Such preferred additives include, but are not limited to, acrylic, urethane or polyester resins or binders, lubricants, waxes, biocides, flame retardants, fillers, pigments, dyes, softeners, post-added surfactants, catalysts, and cross-linking agents. A combination of additives may also be used.

The processes of the invention comprise applying the reaction product of the invention to a textile substrate material as well as a process for the manufacture of the reaction product of the invention. Although the process of manufacture of the invention contains parameters as already described herein, it is preferred that the following particulars be used. For the purposes of description for the following preferred embodiment of the invention, starch and phthalic anhydride are used as examples. First, the starch must be charged to the mixer. Typically the starch has a water content of 7.0 to 12.0% based on the total weight of the starch. The starch is heated in the dry blender until the water content is 6% or less. One example is to heat the starch alone in the heated dry blender to 200°F - 220°F (93°C to 105°C) to approximately 1% or less water content. The agitation is controlled at this step so as to minimize the amount of dust generated in the head space. It is preferred that a vacuum be used to expedite the drying process of the starch by allowing water to be taken from the blender until a water content of 0 - 6.0 % by weight of the total weight (100 weight %) of the starch is obtained, preferably less than 5%, more preferably, 0.01 – 4.0%, and even more preferably 0.01 – 2.0%, most preferably, less than 1.0%. Next, ground phthalic anhydride is added to the extent of 0.2 to 6 weight %, preferably, 1.0 – 5.0 weight %, and more
preferably, 3.0 – 5.0 weight %, and even more preferably, 3.6 – 4.2 weight %, based on 100 weight % total of starch and phthalic anhydride. The mix is heated with agitation at atmospheric pressure to reaction temperature. It is preferred that the reaction time is from 5 to 120 minutes and that the reaction temperature is from 250°F ± 30°F (121°C ± 17°C), preferably, that the reaction time is from 100 to 120 minutes and the reaction temperature is about 250°F (121°C), and more preferably, that the reaction time is from 20 to 30 minutes and the reaction temperature is from 265°F ± 15°F (129°C ± 9°C).

The mixer is then cooled to 100°F to 110°F (38°C to 43°C). The reaction product is neutralized with dilute ammonia in an amount sufficient to react with the unreacted phthalic anhydride, typically from 1-75% of the initial amount charged. The neutralization is mainly performed due to health, safety and/or environmental reasons. It is not necessary for the satisfactory performance of the reaction product.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

**EXAMPLES**

*Example 1.* - The following example illustrates the pilot scale treatment of the preferred aromatic anhydride (phthalic anhydride) with unmodified corn starch. 67.5 pounds of CLINTON 106 corn starch are charged to a Littleford Ploughshare reactor preheated to an incoming steam jacket temperature of about 320°F (160°C). The resultant internal temperature is about 300°F. The ploughblade mixer is started, adjusted to half speed, and the vacuum is initiated while simultaneously heating to 222°F (105°C) at -25 inches of mercury gauge pressure. Once this temperature and
pressure are achieved, a sample is taken. The starch is held at temperature until the water is determined to be 0.5% or less as measured by an electronic water balance. The vacuum is removed, and 2.5 pounds of 65 mesh phthalic anhydride are charged through the stack. Filter bags are placed over the stack, and an internal chopper or baffle blade mixer is turned on. The temperature is raised to 250 – 260°F (121°C - 127°C) over 30 minutes and held for one hour. The steam jacket is blown down, the chopper discontinued, and the product is cooled to 130°F (54°C). Next, 12.6 pounds of 2.2% ammonia are charged by an internal spray head. The product is cooled below 110°F (43°C) and discharged as a free-flowing powder. The resultant pH of a 5% dispersion is 8-9. Adhesion of the acylated starch to MYLAR polyester film is good.

*Example 2.* – The procedure used in Example 1 is repeated, where the anhydride used is trimellitic. Adhesion of the acylated starch to MYLAR polyester film is good.

*Example 3.* – This example illustrates the lab preparation of said acylated starch using a small laboratory version of the Littleford Ploughshare blender. To said mixer, 1148 grams of CLINTON 277 acid-modified corn starch is charged. The vent cover is placed on the top without filter and the starch is agitated slowly while heating up using 13 psig steam pressure. The starch is held at 200 – 220°F (93°C - 104°C) for two hours and effectively 99% dry. The agitation is turned off, and 44.5 grams of ground phthalic anhydride is added to the unit. The vent box is replaced along with cellulose filter screens. The agitation is turned on three-quarter speed and the mixture is heated to 235 – 250°F (113°C - 121°C) and held for two hours. The mixture is cooled to 100°F (38°C) and discharged. Adhesion of the acylated starch to MYLAR polyester film is good.
Example 4. - The procedure used in Example 3 is repeated where the anhydride used is pyromellitic anhydride. Adhesion of the acylated starch to MYLAR polyester film is good.

Example 5. – The product produced by Example 3 neutralized by 2.2% ammonia to pH 3-9. Adhesion to the acylated starch to MYLAR polyester film is good.

Example 6. – The product produced by Example 4 neutralized by 20% triethanolamine to pH 3-9. Adhesion of the acylated starch to MYLAR polyester film is good.

Examples 7–15 (Table 1)

In each of the above examples (1-6) and in each of the examples below (7-15) the acylated starch was slurried in water at 5% solids and heated with good agitation to just below the boiling temperature for 15 minutes to “cook out” the starch, i.e., to heat above the gelatinization temperature of the starch. After the 15 minute hold, the resulting slurry was cooled to about 85°C. Aliquots of the slurry were transferred to and drawn down on a clean sheet of MYLAR polyester film with a 40-mil Bird type film applicator. After drying at room temperature overnight, the adhesion of the starch film to the MYLAR polyester sheet was measured by repeatedly scraping the starch film with a knife blade. (Good adhesion to MYLAR polyester film is taken as an indication that the starch will also have improved adhesion to textile fibers and yarns containing polyester fibers.) The adhesion rating system used was as follows:

1 = poor adhesion
2 = marginal adhesion
3 = fair adhesion
4 = good adhesion
5 = excellent adhesion
### TABLE 1

**Effect of Water Level, Reaction Temperature and Reaction Time on Adhesion to Polyester**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Corn Starch</th>
<th>Starch Type (Alkali Fluidity)</th>
<th>Water, %</th>
<th>Phthalic Anhydride, %</th>
<th>TSP, %</th>
<th>Reaction Temp. °C</th>
<th>Reaction Time, Hr.</th>
<th>Adhesion Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Clinton 106</td>
<td>Pearl (0)</td>
<td>5</td>
<td>4.0</td>
<td>4</td>
<td>60-70</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>Clinton 106</td>
<td>Pearl (0)</td>
<td>5</td>
<td>4.0</td>
<td>0</td>
<td>60-70</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>Clinton 277</td>
<td>Acid-modified (80)</td>
<td>5</td>
<td>4.0</td>
<td>4</td>
<td>60-70</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Clinton 277</td>
<td>Acid-modified (80)</td>
<td>5</td>
<td>4.0</td>
<td>0</td>
<td>60-70</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>Clinton 277</td>
<td>Acid-modified (80)</td>
<td>&lt;1</td>
<td>4.4</td>
<td>0</td>
<td>110-113</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>Clinton 277</td>
<td>Acid-modified (80)</td>
<td>&lt;1</td>
<td>4.4</td>
<td>0</td>
<td>110-113</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>13</td>
<td>Clinton 240</td>
<td>Acid-modified (40)</td>
<td>&lt;1</td>
<td>4.4</td>
<td>0</td>
<td>121-129</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>14</td>
<td>Clinton 277</td>
<td>Acid-modified (80)</td>
<td>&lt;1</td>
<td>4.4</td>
<td>0</td>
<td>121-129</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>15</td>
<td>Clinton 277</td>
<td>Acid-modified (80)</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>Not heated</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

**TSP = trisodium phosphate**

Water % is the weight % of moisture or water present during the solid state reaction based on the total weight of solid state reactants equaling 100% by weight.
Phthalic Anhydride % is the weight % of phthalic anhydride based on the total weight percentage of starch and anhydride or acid equaling 100 weight%.

Alkali Fluidity is a measurement to determine a product's viscosity or change in its molecular weight. This is a viscosity measurement made at room temperature (25°C). In this test, a constant amount of starch, regardless of extent of conversion, is pasted with sodium hydroxide solution for a specified time. The volume of chemically cooked paste that flows through a standard orifice in 70 seconds is its Alkali Fluidity value, measured in milliliters. Unmodified starch has an Alkali Fluidity value of zero indicating no flow through the orifice in 70 seconds. As the starch is converted, its flow value increases. Water alone has an Alkali Fluidity (flow value) of 100 seconds, indicating 100 milliliters delivered through the standard orifice in 70 seconds.

Examples 7 – 10 in Table 1 show that, at a Water % of 5%, there is no beneficial effect on adhesion of the phthalated starch to MYLAR polyester film obtained by including an alkali (TSP) in the solid-state reaction mix. In fact, the inclusion of TSP seems to have a slightly deleterious effect on adhesion.

Examples 11-15 show the beneficial effect of reducing the water level of the starch (acid-modified starch in this case) to much below the 5% level. Reducing the water level to less than 1% improves the adhesion of the resulting phthalated starch from a 3 rating ("fair" adhesion) to a 4 rating ("good" adhesion). Inclusion of an alkali is not required to achieve this improvement.

Examples 13 and 14 illustrate how reaction time can be greatly reduced by increasing reaction temperature by only about 10°C to 15°C.

Example 15 shows, by comparison with Examples 7-14, the poor adhesion to MYLAR polyester substrate of starch that has not been acylated with an aromatic anhydride by the practice of the present invention.

The utility of acylated starches of this invention is demonstrated by sizing a polyester/cotton yarn with a dispersion of the acylated starch in water, drying the yarn and testing the abrasion resistance of the sized yarn. For the examples in Table 2, a 65/35 polyester/cotton yarn (26/1 cotton
count) is sized with the phthalated starches of examples 16-22 and tested for abrasion resistance on a laboratory device that simulates the abrasive action that yarns experience in weaving. The number of abrasion cycles of the machine required to break the yarn is recorded; the greater the number of cycles, the greater the abrasion resistance of the sized yarn.

**TABLE 2**

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<th>Example No.</th>
<th>Starch</th>
<th>Starch Type</th>
<th>Water, %</th>
<th>Reaction Temp., °C</th>
<th>Reaction Time, hr.</th>
<th>Adhesion Rating</th>
<th>Abrasion Cycle</th>
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</table>

Untreated Clinton 106 starch gave 194 Abrasion Cycles

Untreated Clinton 227 starch gave 621 Abrasion Cycles

*4.3 weight % of phthalic anhydride based on total weight of the starch and phthalic anhydride.

Water % is defined as in Table 1.

Examples 16 – 18 show the positive effect of reducing the water content of the starch. Adhesion rating and abrasion resistance (of sized polyester/cotton yarn) increases as initial water level of the starch decreases. The polyester fiber in the polyester cotton yarn used in Examples 16-22 is polyethylene terephthalate or PET polyester. This is the same polyester used to make MYLAR polyester film. No TSP or other alkali is included in the solid state phthalations of Examples 16-22.
Example 23 – Example 20 is repeated except phthalic acid is substituted for phthalic anhydride. The adhesion rating of the resulting acylated starch is 4 and the number of abrasion cycles is 1015.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention. The present invention is further represented by the following claims.
We Claim:

1. A reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, in the absence of a base catalyst, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group.

2. The reaction product of Claim 1 wherein said starch is derived from rice, wheat, tapioca, potatoes, and/or corn.

3. The reaction product of Claim 1 wherein said starch is acid-modified prior to said solid state reaction.

4. The reaction product of Claim 1 wherein said starch is in a granulated form.

5. The reaction product of Claim 1 wherein the number average molecular weight of the starch is 10,000 - 300,000.

6. The reaction product of Claim 1 wherein the number average molecular weight of the starch is 80,000 -120,000.

7. The reaction product of Claim 1 wherein said aromatic anhydride and/or aromatic acid is present in the amount of 0.05 to 6 weight % and wherein the total weight percentage of starch and anhydride or acid equals 100 weight %.
8. The reaction product of Claim 7 wherein said aromatic anhydride and/or aromatic acid is present in the amount of 3.0 to 5.0 weight %.

9. The reaction product of Claim 1 wherein said aromatic anhydride initially has a particle size of 2 mm or less.

10. The reaction product of Claim 1 wherein said aromatic anhydride is selected from the group consisting of trimellitic anhydride, pyromellitic dianhydride and phthalic anhydride.

11. The reaction product of Claim 10 wherein said aromatic anhydride is phthalic anhydride.

12. The reaction product of Claim 1 having a D.S. of 0.001 to 0.10.

13. The reaction product of Claim 7 having a D.S. of 0.001 to 0.07.

14. The reaction product of Claim 1 wherein, during the solid state reaction, said solid state reactants have a total water content of 0 to 6.0 weight % based on a total weight percentage for the solid state reactants of 100% weight %.

15. The reaction product of Claim 14 wherein said solid state reactants have a total water content of 0.1 to 4.0 % weight %.

16. The reaction product of Claim 14 wherein said solid state reactants have a total water content of less than 1.0% weight %.
17. The reaction product of Claim 1 wherein a base is added to the final reaction product to react with unreacted aromatic anhydride or aromatic acid.

18. The reaction product of Claim 17 wherein said base is selected from the group consisting of ammonia, aqua ammonia, amines, polyamines, and aminoalcohols.

19. The reaction product of Claim 1 wherein said at least one starch and said at least one aromatic anhydride and/or aromatic acid are mixed in a dry blender during the reaction.

20. A reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group; and wherein, during said solid state reaction, said solid state reactants have a total water content of 0 to 6.0 weight % based on a total weight percentage.

21. The reaction product of Claim 20 wherein said starch is derived from rice, wheat, tapioca, potatoes, and/or corn.

22. The reaction product of Claim 20 wherein said starch is acid-modified prior to said solid state reaction.

23. The reaction product of Claim 20 wherein said starch is in a granulated form.
24. The reaction product of Claim 20 wherein the number average molecular weight of the starch is 10,000 - 300,000.

25. The reaction product of Claim 24 wherein the number average molecular weight of the starch is 80,000 - 120,000.

26. The reaction product of Claim 1 wherein said aromatic anhydride and/or aromatic acid is present in the amount of 0.05 to 6 weight % and wherein the total weight percentage of starch and anhydride or acid equals 100 weight %.

27. The reaction product of Claim 20 wherein said aromatic anhydride and/or aromatic acid is present in the amount of 3.0 to 5.0 weight %.

28. The reaction product of Claim 20 wherein said aromatic anhydride initially has a particle size of 2 mm or less.

29. The reaction product of Claim 20 wherein said aromatic anhydride is selected from the group consisting of trimellitic anhydride, pyromellitic dianhydride and phthalic anhydride.

30. The reaction product of Claim 20 wherein said aromatic anhydride is phthalic anhydride.

31. The reaction product of Claim 20 having a D.S. of 0.001 to 0.10.

32. The reaction product of Claim 20 having a D.S. of 0.001 to 0.07.
33. The reaction product of Claim 20 wherein said solid state reactants have a water content of less than 5.0% by weight.

34. The reaction product of Claim 20 wherein said solid state reactants have a total water content of 0.1 – 4.0% by weight.

35. The reaction product of Claim 20 wherein said solid state reactants have a total water content of less than 1.0% by weight.

36. The reaction product of Claim 20 wherein said at least one starch and said at least one aromatic anhydride and/or aromatic acid are mixed in a dry blender during the reaction.

37. A textile sizing agent comprising the reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, in the absence of a base catalyst, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group.

38. A textile sizing agent comprising the reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group; and wherein, during said solid state reaction, said solid state reactants have a total water content of 0 to 6.0 weight % based on a total weight percentage of 100 weight%.
39. A textile sizing agent for polyester fibers and polyester-containing yarn comprising the reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, in the absence of a base catalyst, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group.

40. A textile sizing agent for polyester fibers and polyester-containing yarn comprising the reaction product of at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group; and wherein, during said solid state reaction, said solid state reactants have a total water content of 0 to 6.0 weight % based on a total weight percentage of 100 weight%.

41. A textile yarn sized with the textile sizing agents of Claims 37 and 38.

42. The textile yarn of Claim 41 comprising one or more polyesters.

43. The textile yarn of Claim 42 wherein said one or more polyesters comprise 80 to 100 mole% terephthalic acid residues and 100 to 80 mole % ethylene glycol wherein the total mole percentages of the
glycol component equals 100 mole % and the total mole percentages of the acid component equals 100 mole %.

44. The textile yarn of Claim 43 comprising poly(ethylene terephthalate).

45. The textile yarn of Claim 42 wherein said one or more polyesters comprise 80 to 100 mole% terephthalic acid residues and 100 to 80 mole % 1,4-cyclohexanediylmethanol wherein the total mole percentages of the glycol component equals 100 mole % and the total mole percentages of the acid component equals 100 mole %.

46. The textile yarn of Claim 42 wherein said one or more polyesters comprise 80 to 100 mole% terephthalic acid residues, 10 to 50 mole % 1,4-cyclohexanediylmethanol residues, and 90 to 50 mole % ethylene glycol residues, wherein the total mole percentages of the glycol component equals 100 mole % and the total mole percentages of the acid component equals 100 mole %.

47. The textile yarn of Claim 41 comprising a blend of polyester fibers and fibers selected from the group consisting of cotton, polyacryls, polyolefins, rayons, and wool.

48. A process for sizing a textile substrate material comprising applying to the textile material a composition comprising the reaction product of Claims 1 and 20.

49. The process of Claim 45 wherein said textile substrate material comprises one or more polyesters.
50. The process of Claim 49 wherein said one or more polyesters comprising 80 to 100 mole% terephthalic acid residues and 100 to 80 mole% ethylene glycol wherein the total mole percentages of the glycol component equals 100 mole % and the total mole percentages of the acid component equals 100 mole %.

51. The textile yarn of Claim 49 wherein said one or more polyesters comprise 80 to 100 mole% terephthalic acid residues and 100 to 80 mole% 1,4-cyclohexanediol wherein the total mole percentages of the glycol component equals 100 mole % and the total mole percentages of the acid component equals 100 mole %.

52. The textile yarn of Claim 49 wherein said one or more polyesters comprise 80 to 100 mole% terephthalic acid residues, 10 to 50 mole% 1,4-cyclohexanediol residues, and 90 to 50 mole% ethylene glycol residues, wherein the total mole percentages of the glycol component equals 100 mole % and the total mole percentages of the acid component equals 100 mole %.

53. The process of Claim 49 comprising a blend of polyester fibers and fibers selected from the group consisting of cotton, polyacrylics, polyolefins, rayons, and wool.

54. The process of reacting at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, in the absence of a base catalyst, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group.
55. The process of reacting at least one starch with at least one aromatic anhydride and/or aromatic acid wherein said starch is reacted in the solid state with solid state reactants comprising said aromatic anhydride and/or aromatic acid, and at a time and temperature sufficient to obtain a reaction between said anhydride and/or acid and said starch(es) to form an ester substituent group; and wherein, during said solid state reaction, the solid state reactants have a total water content of 0 to 6.0 weight % based on a total weight percentage of 100 weight%.

56. The process of Claim 55 wherein said starch and aromatic anhydride or aromatic acid are dried prior to the solid state reaction to a water content of 0.1 to 4.0 weight %.

57. The process of Claim 56 wherein said starch and aromatic anhydride or aromatic acid are dried prior to the solid state reaction to a water content of less than 1 weight %.

58. The process of Claim 56 wherein said starch and aromatic anhydride or aromatic acid are dried under vacuum where said temperature is increased to the initial reaction temperature.
## INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C08B31/04 C08B33/02 C08B35/02 D06M15/11

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08B D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

BEILSTEIN Data, CHEM ABS Data, EPO-Internal, PAJ, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>US 4 011 392 A (GLOWAKY RAYMOND CHARLES ET AL) 8 March 1977 (1977-03-08) abstract; claims 1,11; figure IIIB</td>
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<td>US 3 981 833 A (LARK JOHN C) 21 September 1976 (1976-09-21) column 4, line 3 - line 18 column 1, line 30 - line 34</td>
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Further documents are listed in the continuation of box C. 

Patent family members are listed in annex.

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**Date of the actual completion of the international search**

2 June 2003

**Date of mailing of the international search report**

11/06/2003

**Name and mailing address of the ISA**

European Patent Office, P. B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 940-2060, Tx. 31 651 eop nl Fax. (+31-70) 940-3016

**Authorized officer**

Schütte, M
**INTERNATIONAL SEARCH REPORT**

**Application No:** PCT/US 03/04083

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