United States Patent

Doerr et al.

[15] **3,692,880**

[45] **Sept. 19, 1972**

[54] **PHOSPHATED POLYOLS AND PROCESS FOR MAKING SAME**

[72] Inventors: **Richard L. Doerr**, Orange; **Stephen Fuzesi**, Hamden, both of Conn.

[73] Assignee: **Olin Corporation**

[22] Filed: **May 4, 1970**

[21] Appl. No.: **34,606**

[52] **U.S. Cl.**.....**260/929**, 117/151 L, 117/161, 260/67.6, 260/70, 260/920, 260/928, 260/980

[51] **Int. Cl.**.....**C07f 9/08**, D06m 1/100

[58] **Field of Search**.....260/920, 929, 980, 928

[56] **References Cited**

UNITED STATES PATENTS

3,275,667 9/1966 Bohnunek.....260/929 X

Primary Examiner—Lewis Gotts
Assistant Examiner—Anton H. Sutto
Attorney—Gordon D. Byrkit, Donald F. Clements, Thomas P. O'Day and F. A. Iskander

[57] **ABSTRACT**

A novel phosphated polyol is provided which is used in conjunction with aminoplast resins to provide improved soil release particles to cellulosic fibers and blends of cellulosic fibers with polyester fibers having durable press or wash and wear characteristics.

4 Claims, No Drawings

PHOSPHATED POLYOLS AND PROCESS FOR MAKING SAME

This invention relates to novel textile treating compositions, the method of preparing and applying such compositions and to textile materials treated therewith. More specifically, the invention relates to compositions and textile treatments which provide improved soil release properties to textiles.

Cellulosic fibers, including cotton, linen, jute, flax and regenerated cellulose fibers, including viscose rayon, in the form of staple, yarn and fabrics have generally satisfactory soil release properties.

The term "soil release" refers to the ability of the fiber to be washed to remove soil and particularly oily materials in contact with said fibers. The present invention promotes the removal of soil from fibers and renders fabrics more amenable to cleansing by washing.

A further feature of the present invention is the prevention of soil redeposition from the wash water. During washing and rinsing, the soil has a tendency to redeposit on the fibers from the wash water or rinse water. The soil release ability of fibers treated according to the present invention also prevents redeposition of soil removed in the washing.

The introduction of blends of cotton with synthetic fibers has aggravated the problem of soil release and redeposition. The synthetic fibers, particularly the polyester fibers, for example, those prepared from poly(ethylene terephthalate), have many desirable properties which have made them commercially acceptable for many end uses, both alone and in various combinations with natural fibers. However, the soil release properties of the polyester fibers are much poorer than those of the cellulosic fibers. The polyester fibers are hydrophobic rather than hydrophilic. They attract and hold the soil more tenaciously than cellulosic fibers and hinder the ingress of water necessary for cleaning the fabric.

The problem of soil release and redeposition has been further compounded by durable press and wash-and-wear treatments which render the cellulosic fibers in textiles and blends less hydrophilic. These finishing treatments usually consist of impregnating and reacting the cellulosic fibers with aminoplast resins having N-methylol groups, e.g., urea-formaldehyde resins, cyclic urea-formaldehyde resins, especially dihydroxy dimethylol ethyleneurea resins. The fibers subjected to such treatments retain the soil more tenaciously than the untreated cellulosic fibers, lose much of their soil release properties and are more subject to redeposition of soil. Oily soils accepted and retained by garments of these fibers, when worn, are difficult to remove in normal washing machine operations. Even relatively clean garments containing these treated fibers tend to pick-up soil from the dirty wash water. As a result, oily soil spots are never completely removed from these garments by washing. Repeated washings intensify the effects of soil pick-up from the dirty wash water with increasing overall grey or yellow discoloration. Eventually the garment becomes unsightly before it is worn out.

Soil release agents presently available do not provide fibers with adequate levels of initial and durable soil release properties when the fibers have been subjected to durable press or wash-and wear finishing.

Present soil release agents based on polymeric derivatives of acrylic acid are disclosed, for example, in U.S. Pat. No. 3,090,704 directed to a methyl methacrylate-sodium styrene sulfonate-glycidol methacrylate terpolymer and U.S. Pat. No. 3,377,249 directed to a process in which the active soil release agent is a copolymer of ethyl acrylate and acrylic acid in a 70:30 ratio. Problems which still remain when known soil release agents are used with cellulosic textiles, including blends with polyesters, which have been finished with aminoplast resins include:

1. Unsatisfactory initial soil release effect.
2. Poor durability of soil release properties to repeated washings.
3. Poor compatibility with the magnesium chloride or zinc nitrate catalysts commonly used in aminoplast resin finishing compositions.
4. Require a two-bath process instead of a single bath application for best results.
5. Acrylate emulsions tend to precipitate on standing. Some have poor freeze-thaw stability.
6. Acrylate soil release emulsions tend to form gritty deposits on fabric pad rolls during application which causes problems when picked off by the fabric.

The present invention is primarily directed to the treatment of cellulosic fabrics and to fabrics containing a substantial portion of synthetic polyester fibers. These fibers are generally formed into fabrics which are knitted, woven or non-woven. However, the advantages of this invention can be acheived by treating the fibers, yarns, or threads employed to produce these fabrics. Moreover, and more specifically, the process of the present invention is preferably used for treating textile materials containing cellulosic fibers or blends of polyester and cellulosic fibers to confer durable press or minimum care characteristics and improved soil release properties. The fabrics are suitably formed from a mixture of polyester, e.g., poly(ethylene terephthalate) fibers and cotton or rayon fibers. Textile materials containing only cellulosic fibers are also within the scope of the present invention.

Surprisingly, it has now been discovered that the above mentioned problems and deficiencies are substantially eliminated by combining phosphated polyoxyalkylene ester of phosphoric acid with an aminoplast textile resin and an aminoplast resin catalyst, applying the mixture to the textile and subjecting the treated textile to resin curing conditions. The invention contemplates the phosphated product, the finishing composition combining the phosphated product and the aminoplast resin, catalyzed and uncatalyzed, the process of treating fibers with the treating composition and the fibers and textiles thus treated.

Advantages of the present invention are:

1. An improved level of initial soil release effect on treated fabric.
2. An improved level of durable soil release effect on treated fabric after multiple washings.
3. Improved compatibility with the magnesium chloride and zinc nitrate textile resin catalysts commonly used in aminoplast textile resin formulations.
4. A single bath process that increases rate of production and is more economical than a two-bath process.

5. A completely homogeneous water-soluble finishing composition not subject to separation or freeze-thaw instability.
6. No undesirable product build-up on fabric pad rolls during application.

The phosphated soil release agent is prepared by (1) oxyalkylating 100 percent phosphoric acid with two to 10 moles of alkylene oxide, suitably propylene oxide or mixtures with up to 50 percent by weight of ethylene oxide to form a polyol and (2) reacting the resulting polyol with phosphoric acid or phosphoric anhydride.

Minor amounts, from 2 to 25 percent by weight of the alkylene oxide mixture is suitably other alkylene oxides of two to four carbons, for example, alpha- or beta-butylene oxide, trichlorobutylene oxides, glycidol and epichlorohydrin. The oxides are also suitably reacted with 100 percent phosphoric acid in block type as well as random type polymers.

The oxyalkylated phosphoric ester (polyol) is suitably phosphated with phosphoric anhydride or phosphoric acid containing at least 85 percent H_3PO_4. Suitable molar ratios of polyol per phosphorus atom in the phosphating agent are from 0.5:1 to 2.2:1 and preferably from 0.75:1 to 1.5:1. The preferred phosphating agent is phosphoric anhydride which gives the most effective and durable soil release agent.

The reaction of the polyol with the phosphating agent is carried out at temperatures up to 150° C. under pressures of atmospheric or below, e.g., from 5 to 780 mm. Thorough mixing of the polyol with the phosphating agent, particularly phosphoric anhydride, is advantageous to provide sufficient initial reaction to solubilize most of the phosphoric anhydride in the polyol, sufficient reaction time and temperature to essentially complete the reaction, followed by filtration to remove any small amounts of undissolved solids. The rate of reaction is temperature dependent but it proceeds even at 20° C. or below. The rate of reaction is accelerated by increasing the temperature, but color formation increases above about 70° C. The temperature range is suitably from 0° C. to 150° C. with very long reaction time at low temperatures and very short reaction time at high temperatures. The preferred range is 30°–80° C. for 15 minutes to 1 week.

The resulting phosphated polyols are clear, light amber colored, highly viscous liquids at room temperature. Yields are about 90 to 95 percent. Hydroxyl numbers vary from about 140 to 190. The acid numbers show values of about 190 and 250 (two breaks). The pH of a 20 percent solution in distilled water is from 0.5 to 1.0. Viscosity at 70° C. is from 20,000 to 40,000 CPS.

The phosphated polyol thus prepared is used in conjunction with an aminoplast resin composition for treating textiles. Suitable resins are the well-known, commercially available aminoplasts, for example, N-methylol compositions based on urea-formaldehyde, cyclic urea-formaldehyde and especially dihydroxy dimethylol ethyleneurea resins. Catalysts usually added to these resins are metal salts of the formula MX_2 where M is magnesium or zinc and X is chloride or nitrate, particularly, magnesium chloride or zinc nitrate. Usually from 1 to 15 percent of the catalyst, based on the weight of the resin is suitable.

The proportion of phosphated polyol added to the aminoplast composition is usually about 2 to 10 percent based on the total weight of the formulation. In use, the mixture of phosphated polyol and aminoplast, including catalyst, is applied to the fiber or textile to be treated and cured under conditions usual for applying and curing the aminoplast finishing compositions, that is, at temperatures of about 300° to 400° F. for 0.1 to 15 minutes.

EXAMPLE I

A. Preparation of 100 percent Phosphoric Acid

Initiator for the polyol was 100 percent phosphoric acid prepared from commercial 105 percent phosphoric acid by the addition of one part of distilled water to 20.5 parts of 105 percent phosphoric acid. The water was added to the acid with agitation, maintaining the temperature of the mixture at 24 to 40° C. After the addition was completed, the mixture was heated at 85° C. for 2 hours.

B. Preparation of Polyol

The 100 percent phosphoric acid prepared in Example I.A. was oxyalkylated in a 100 gallon reactor formed of 304 stainless steel fitted with an agitator and equipped to add the alkylene oxide below the surface of the liquid in the reactor. Both acid feed and oxide feed were introduced into the reactor under nitrogen pressure through flow meters and check valves.

The reactor initially contained 12 pounds of a finished product from a previous batch. The oxide used was a mixture of propylene oxide and ethylene oxide in a ratio of 90:10 by weight. During a period of about 28 hours, the acid and oxide were introduced using a higher proportion of the acid, based on the total to be introduced, than the proportion of oxide. The molar ratio of oxide to acid initially was 1.44:1 which rose to 4.33:1 in the final product. During the addition of the reactant, the temperature, initially at 10° C. rose to 70° C. and the pressure varied from 16 to 27 psig. The total weight of acid introduced was 117 pounds and the total oxide was 507 pounds. Subsequently at 70° C., an additional 136 pounds of the oxide mixture was introduced in four portions with a holding period of 2 to 4 hours at 70° C. after each addition. The final pH was 5.8. After completion of the reaction, unreacted oxide was stripped by heating the mixture for 3 hours at 75° C. under pressures from 10 to 25 mm. The product amounted to 631 pounds or 79.3 percent based on the material charged.

C. Reaction of Polyol with Phosphoric Anhydride

A portion of 190 parts by weight of the polyol prepared in Example I.B. having a hydroxyl number of 303 and a molecular weight of 555.5 was charged to a well-stirred reactor followed by 42 grams of phosphoric anhydride. The mixture was maintained at 20° to 30° C. for 2 hours by cooling and then the temperature rose to 60° C. during 3 hours. The mixture was maintained with stirring at atmospheric pressure and at 60° C. for an additional 7.5 hours, filtered and cooled.

D. Formulation Preparation

Five grams of the product from Example I.C. was weighed into a 250 ml. breaker and dissolved in 19 grams of distilled water. The pH of the aqueous solution was adjusted to 7.0 on a Beckman Glass Electrode pH Meter by the slow addition of 10 percent aqueous sodium hydroxide solution (7 g.) using good agitation. To the neutralized solution was added 13 grams of "-

Permafresh LF," a dimethylol cyclic urea compound, 1 gram of "Polymel CC," a polyethylene emulsion softener and 5 grams of 20 percent by weight ageuous magnesium chloride solution. The final formulation had a pH of 5.9.

E. Formulation Application

A 5 × 8 inches swatch of 65/35 Dacron/cotton shirting fabric was thoroughly wetted in the formulation prepared in Example I.D. Excess solution was removed from fabric by passing the open width through pressurized rubber squeeze rolls to give approximately 60 percent wet pick-up of the formulation on the dry weight of the goods. The impregnated fabric was dried at 110° to 120° C. for 90 seconds and then cured at 159°–161° C. for 180 seconds.

F. Soil Release Evaluation

The cured fabric, after 30 minutes at ambient temperature and humidity, was soiled with 10 drops of dirty motor oil centrally distributed over a 2 to 4 square inch area. The oil was allowed to soak into the fabric for 30 minutes and then it was washed in a Tergotometer at 50°–55° C. for 20 minutes using 1.5 grams of "Tide" in 1 liter of water. The washed fabric was rinsed in warm water and dried on a line. The dried fabric was rated for soil release visually by placing the sample on a white cardboard background and observing the color intensity of any remaining dirty motor oil soil. The fabric of this example gave complete soil release of the dirty motor oil. The same type of fabric finished with 10 percent "Rhoplex SR-488," a commercial acrylic type soil release agent, in a conventional two-bath application and soiled and washed in the previously described manner, did not give complete soil release of dirty motor oil. The soiled area was clearly visible after washing. Other portions of the same fabrics washed prior to soiling still show the superior soil release properties of the product of this invention applied in a single bath over "Rhoplex SR-488" applied by a two-bath application.

Reflectance was also measured after soiling with dirty motor oil and washing, as described above, using a Photovolt reflectometer with a blue filter. The reflectance of the treated cloth was 76 initially after soiling and one washing. Another treated swatch was washed 5 times, soiled and washed again. Reflectance was 63, showing excellent durability.

EXAMPLE II

A. Preparation of Polyol

Propylene oxide and 100 percent phosphoric acid, prepared as described in Example I.A. were introduced into a nitrogen padded reactor cooled externally with ice water. A reflux condenser cooled with dry ice was provided. The mixture was vigorously stirred. The feed of propylene oxide was started first and a weight ratio of propylene oxide to phosphoric acid of at least 5:1 was maintained. The rates of addition of acid and oxides were adjusted to maintain the reaction temperature at 20° to 30° C. During 2 hours, a total of 50 grams of 100 percent phosphoric acid and 250 grams of propylene oxide was introduced. Finally the reaction mixture was stirred at 25° to 30° C. for 6 hours. The product amounted to 295 grams.

The reaction mixture was purged with a stream of dry nitrogen and refluxed for 4 hours at 54° C. then excess oxide was to to escape and the reflux temperature to rise ot 70° C. and this temperature was maintained for 4 hours. Finally the mixture was stripped at 70° C. for 2 hours under a pressure of 10 mm.

B. Reaction of Polyol with Phosphoric Anhydride

A mixture of 190 grams of the polyol prepared in Example II.A. and 42 grams of phosphoric anhydride was stirred under nitrogen for 3.25 hours at temperatures from 25° to 45° C. The pressure was then reduced to 10 mm. and the temperature was raised to 70° C. during a period of 0.65 hours. The reaction mixture was maintained at that temperature for a total of 8 hours. The mixture was filtered and cooled. It mounted to 160 grams or about 70 percent based on the materials charged.

The product was formulated and applied to Dacron-cotton fabric as described in Example I. The reflectance was measured using a Photovolt reflectometer with a blue filter. The reflectance for the treated cloth after soiling and washing was 75. Another treated swatch was washed 5 times, soiled and washed again. Reflectance was 61, showing excellent durability.

EXAMPLE III

A. Preparation of 100 percent Phosphoric Acid

Crystallized 100 percent phosphoric acid was obtained by cooling 100 percent phosphoric acid, prepared as described in Example I.A., with dry ice to start crystallization and then holding the mixture at 35° C. for several hours. The crystals were filtered from the liquor.

B. Preparation of Polyol

To 50 ml. of a mixture of propylene oxide and ethylene oxide in a weight ratio of 90:10 was added, during a period of 1.5 hours, a total of 50 grams of melted, previously crystallized 100 percent phosphoric acid, prepared as described in Example III.A., and 250 grams of oxide mixture, maintaining the weight ratio of oxide to acid between 5:1 and 6:1. A reflux condenser cooled with dry ice prevented the escape of alkylene oxide. After the addition was complete, the reaction mixture was maintained at 20° to 30° C. for 2 hours and then stood over night. Subsequently, the reaction mixture was heated during a period of 4 hours until the reflux temperature reached 70° C. where it was maintained for 2 more hours. Finally the product was stripped for 2 hours at 70° C. under 10 mm. pressure. The yield of phosphated polyol was 244 grams.

C. Reaction of Polyol with Phosphoric Anhydride

To 190 grams of the product of Example III.B., maintained under nitrogen, 42 grams of phosphoric anhydride was added at 20° C. with vigorous agitation. After the addition was complete, the mixture was stirred under nitrogen at 20° C. for 1 hour. The temperature was then gradually raised to 70° C., reducing the pressure to 10 mm. The mixture was maintained at this pressure with stirring for 8 hours. The product was filtered, yielding 170 grams or 73 percent based on the materials charged.

Formulated, applied and tested as described in Example I, the reflectance of the Dacron-cotton was initially 74 and after five washings was 60.

EXAMPLE IV

A. Preparation of Polyol

The polyol was prepared from 50 grams of 105 percent phosphoric acid and 250 grams of propylene oxide reacted as described in Example III.B. Total reaction time at 70° C. was 2 hours. The phosphated polyol product amounted to 232 grams or 77 percent based on the starting material.

B. Reaction of Polyol with Phosphoric Anhydride

A mixture of 190 grams of the product of Example IV.A. and 40 grams of phosphoric anhydride was reacted as described in Example II.B. at temperatures up to 70° C. for a period of 7 hours. The mixture was finally heated to 95° C. for 2 hours under 10 mm. pressure filtered hot. The product, filtered hot, amounted to 150 grams.

Formulated, applied and tested as described in the preceding examples, the product showed initial reflectance of 75 and a reflectance of 62 after five washings.

EXAMPLE V

A. Preparation of Polyol

In the manner of the preceding examples, 150 grams of 100 percent phosphoric acid was reacted with 550 grams of distilled propylene oxide during a period of 5 hours. An additional 150 grams of propylene oxide was slowly added with agitation at 60° to 70° C. under nitrogen. The mixture was cooled to room temperature and later reheated to 70° C. An additional 150 grams of propylene oxide was added and the mixture was maintained at 80° C. for 6 hours. The mixture was stripped at 80° C. under 10 mm. pressure to yield 700 grams of polyol or 89 percent based on the materials charged.

B. Reaction of Polyol with Phosphoric Anhydride

A total of 190 grams of the product of Example V.A. and 42 grams of phosphoric anhydride were reacted for 11 hours at temperatures up to 70° C. under a pressure of 10 mm. The mixture was filtered to obtain the phosphate polyol product.

Formulated, applied and tested as described above, the reflectance initially was 75 and the reflectance after five washings was 58.

EXAMPLE VI

A. Reaction of Polyol with Phosphoric Anhydride

During a period of 15 minutes, 42 grams of phosphoric anhydride was added to 190 grams of vigorously stirred polyol prepared as described in Example I.B., all under an atmosphere of dry nitrogen and at a temperature of 20° to 30° C. Then 50 ml. of tetrahydrofuran was added slowly which greatly reduced the viscosity of the mixture. Stirring was continued at 20° to 30° C. for 20 hours and then the temperature was raised gradually to 66° C. where it was maintained for 5 hours. The resulting phosphated polyol product was vacuum filtered to clarify and to remove the tetrahydrofuran.

Formulated, applied and tested as described in Example I, the reflectance initially was 78 and after five washings was 63.

EXAMPLE VII

A. Preparation of Polyol

The polyol was prepared in a manner similar to the procedure described in Example I.B. but using 100 percent propylene oxide as the oxyalkylating agent. The polyol had a hydroxyl number of 396 and a molecular weight of 455.

B. Reaction of Polyol with Phosphoric Acid (85 percent)

A mixture of 190 grams (0.42 moles) of the polyol prepared in Example VII.A. and 57.5 grams (0.5 mole of H_3PO_4) in the form of 85 percent phosphoric acid was heated for 4 hours at 120° to 125° C. under aspiration vacuum (about 20 mm.) with nitrogen padding and good stirring. The product amounted to 217 grams or 94 percent of theory.

C. Formulation Preparation

5 grams of the product form Example VII.B. was dissolved in 26 ml. of distilled water. Sodium hydroxide solution (10 percent) was added to raise the pH to 4.0. To the partly neutralized solution was added 2.5 grams of SR 525X, a bath stabilizer, 12.5 grams of Permafresh LF (dimethylol dihydroxy ethyleneurea), 1 gram of Polymel CC, a polyethylene emulsion softener and 3 grams of magnesium chloride catalyst solution (35 percent).

D. Formulation Application

Two 5 inches by 5 inches test pieces of 65/35 Dacron/cotton blended fabric were impregnated with the formulation prepared in Example VII.C. The swatches were squeezed to 80 percent wet pick-up and hung on a line to dry for 2 hours. The impregnated swatches were cured at 160° C. for 3 minutes.

E. Soil Release Evaluation

One drop of oxidized olive oil was placed on each swatch and allowed to stand for 4 hours forming a deep yellow stain about 1 inch in diameter. The fabric was then washed for 15 minutes at 50° C. using 2 grams per liter of Tide in a Tergotometer and then rinsed. The deep yellow stain was completely removed.

EXAMPLE VIII

A. Reaction of Polyol with Phosphoric Acid (100 percent)

A mixture of 190 grams (0.42 moles) of the polyol prepared as described in Example VII.A. and 49 grams (0.5 moles of H_3PO_4) added as 100 percent phosphoric acid was heated to 125° C. under a pressure of 7 mm. for about 1 hour.

B. Formulation Preparation

A solution of 30 grams of the product of Example VIII.A. in 30 grams of distilled water was neutralized to a pH of 6.5 by adding aqueous sodium bicarbonate solution. The formulation was completed by adding to the neutralized phosphated polyol the ingredients of the textile finishing formulation as described in Example VII.C.

This formulation was applied to a Dacron/cotton fabric and evaluated as described in Example VII substituting dirty motor oil for the oxidized olive oil. After washing only a trace of the stain remained.

What is claimed is:

1. Method of preparing a phosphated polyol having hydroxyl number from about 140 to 190 and acid number from about 190 to 250 by (1) oxyalkylating phosphoric acid at a temperature of from 0° to 100° C with an alkylene oxide selected from the group consisting of propylene oxide and mixtures containing at least 50 percent by weight of propylene oxide, balance alkylene oxides having two to four carbons, the molar

ratio of said oxides to said phosphoric acid being from 2:1 to 10:1 and (2) heating the resulting polyol at temperatures from 30° to 150° C. under pressures not exceeding atmospheric with a phosphating agent selected from the group consisting of phosphoric anhydride and phosphoric acid containing at least 85 percent H_3PO_4, the molar ratio of said polyol to each phosphorus atom in said phosphating agent being from 0.5:1 to 2.2:1.

2. The product of the process of claim 1.

3. Method as claimed in claim 1 in which said oxide is propylene oxide.

4. Method as claimed in claim 1 in which said oxide is a mixture of propylene oxide and ethylene oxide in a weight ratio of at least about 50/50.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,692,880 Dated September 19, 1972

Inventor(s) Richard L. Doerr and Stephen Fuzesi

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

Abstract, line 3, "particules" should read --properties--

Column 6, line 1, "to" should read --allowed to--.

Column 6, line 2, "ot" should read --to--.

Column 6, line 13, "mounted" should read --amounted--.

Signed and sealed this 13th day of February 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents