Qualitative Test for Distinguishing Tris(1-aziridinyl)-Phosphine Oxide (APO) and Tetrakis(hydroxymethyl)Phosphonium Chloride

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▶ A qualitative paper chromatographic test for distinguishing two flame-retardant compounds, tris(1-aziridinyl)phosphine oxide (APO) and tetrakis(hydroxymethyl)phosphonium chloride (THPC), was developed. Using butanol–hydrochloric acid as an eluent, and placing the paper in ammonia fumes, APO develops a yellow color at R_f 0.8 and THPC develops a blue color at R_f 0.4. The method is also suitable for identifying the compounds when present in typical formulations used for impregnating textiles. Test results for APO-, APO–THPC-, and THPC-treated fabrics after curing are described and the last two compared to results obtained with other phosphorus-containing flame-resistant finishes.

TRIS(1-AZIRIDINYL)PHOSPHINE OXIDE, $(\overline{CH_2CH_2N})_3P{=}O$ (*1*), and tetrakis-(hydroxymethyl)phosphonium chloride, $(HOCH_2)_4PCl$ (*3*), are used in textile finishes. The latter, known as THPC, is used as a flame retardant in combination with either methylol melamine or with tris(1-aziridinyl)phosphine oxide, known as APO (*5*). APO is also used to to impart wrinkle resistance to cotton fabrics (*2*).

In evaluating the uses of these two compounds in flame-resistant treatments for military fabrics, an analytical method was developed to distinguish the two when present either in typical finishing bath formulations or on treated fabric. The test, a horizontal paper chromatographic method, consists of spotting the paper with a sample of the compound, the bath formulation, or the acid extract from treated fabric. Distinguishing colors are developed with ammonium molybdate.

REAGENTS

The elutent was a solution of 20% 6*N* HCl and 80% butanol (by volume).

The ammonium molybdate solution for color development was prepared as follows: A solution of 117 grams of 85% molybdic acid, 300 ml. of water, and 120 ml. of concentrated ammonium hydroxide was diluted to a total volume of 800 ml. and allowed to cool. This was added to a solution of 500 ml. of concentrated nitric acid which had been diluted to 1200 ml. Three or four drops of 10% sodium phosphate solution were added and allowed to settle. The solution was filtered before use. The ammonium molybdate solution is the same as that used in phosphorus determinations.

PROCEDURE

A circle of filter paper (Whatman No. 3 for paper chromatography) slightly larger in diameter than the Petri dish (approximately 6-inch diameter) was used. The paper had a $^1/_4$-inch wide wick cut to the center. The solution being tested was transferred to the paper with a micropipet using approximately 125 μl. With its wick immersed in the elutent, the spotted paper was placed in the Petri dish and covered with another Petri dish.

After the elutent had covered approximately two thirds of the area of the Petri dish, the paper was removed and the outside edge of the solvent was marked with a pencil. The paper was air-dried. A few milliliters of the ammonium molybdate solution were poured onto the paper, which was then placed in ammonia fumes from concentrated ammonium hydroxide. The resulting color reactions and R_f values are listed in Table I. The values shown are an average of 10 determinations and the average deviation.

When treated fabric was to be tested, an acid extract was made. To do this, approximately 5 to 10 grams of the fabric were placed in a 400-ml. beaker and 300 ml. of 1% hydrochloric acid were added. The solution was boiled until the volume was reduced to approximately 50 ml. This was used to spot the paper.

DISCUSSION OF RESULTS

A THPC flame-resistant formulation for treating textiles contains, in addition to THPC, triethanolamine, urea, a wetting agent such as isooctylphenoxy(polyethoxy)ethanol and methylol melamine resin. An APO-THPC formulation contains triethanolamine and a wetting agent such as benzyldimethylstearylammonium chloride. None of these other compounds present in the bath formulation interferes with the test. However, there are other phosphates that would give a yellow ring at R_f 0.8. Ammonium phosphate, sodium phosphate, and hexamethyl phosphoramide, for example, will give a yellow ring at R_f 0.8. On the other hand, tris(β-chloroethyl)phosphate, dimethyl hydrogen phosphite, tricresyl phosphate, tris(2-ethylhexyl)phosphate, and trioctyl phosphate produce no color reaction by the test method. The above compounds that do give a yellow ring at R_f 0.8 are not usually encountered in durable flame-resistant finishes.

Table I. R_f Values and Color Reactions of APO and THPC with Molybdate Solution

Compound	R_f	Color
Monomer or Its Finishing Bath Formulation		
APO	0.77 ± 0.02	Yellow
THPC	0.44 ± 0.03	Blue
Acid Extract (1% HCl) of Treated Fabric		
APO	0.76 ± 0.02	Yellow
APO-THPC	0.76 ± 0.02	Yellow
THPC	...	No color

The blue color that forms with the THPC may be due to the reaction product of THPC with ammonia, a white water-insoluble compound. To demonstrate this, THPC was placed in a solution of ammonium hydroxide and the water-insoluble precipitate was filtered and washed. This compound gave the blue color with ammonium molybdate without the necessity of placing the paper in ammonia fumes. The compound did not migrate in the test procedure using the butanol-acid solvent, but remained at the point of origin.

Heating the APO-THPC bath formulation to 50° C. for 1 hour produced no change in the position or color of the two compounds in the chromatogram.

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However, heating the bath formulation to 100° C. made a difference. No color developed at 0.4 but a blue color appeared at the point of origin on the paper. This spot at the origin also gave the molybdenum blue color before the paper was placed in the ammonia fumes. This suggests that in the APO-THPC formulations used for treating cotton the THPC is converted into an insoluble polymer only when heated but remains in the bath formulation as THPC.

In regard to the yellow color with APO, the addition of APO to an ammonium molybdate solution forms a yellow precipitate.

The reaction is highly exothermic and the addition of concentrated solutions of APO to ammonium molybdate should be avoided. The APO molybdate was filtered and titrated with sodium hydroxide according to the usual procedure for a phosphorus determination. Each mole of APO took 5.5 to 5.9 moles of sodium hydroxide. The infrared spectra of the precipitate differ from those of the molybdate formed by sodium phosphate, in that an intense absorption at 7.25 microns in the spectra of the latter is absent in the APO molybdate spectra. On standing, the color of the precipitate changes from yellow to green, which is the same type of color change produced by mixing a reducing agent with ammonium phosphomolybdate.

The infrared spectrum of the molybdate that forms from the acid-extracted APO-THPC–treated fabric is the same as for ammonium phosphomolybdate. The completely polymerized APO, a white water-insoluble solid, does not form a molybdate and does not migrate during the chromatographic test described. However, when the polymerized APO is boiled in 1% hydrochloric acid, it dissolves and the solution will form a yellow ring at R_f 0.8 in the test.

Other phosphorus-containing flame-resistant cotton fabrics were extracted with 1% hydrochloric acid and chromatograms were run. These included phosphorylated cotton and cotton treated with diallylcyanoethane phosphonate, the bromoform adduct of triallyl phosphate in combination with THPC, and chloroethylene (vinyl chloride)–antimony oxide in combination with THPC. Of these, only phosphorylated cotton gives the same yellow ring at R_f 0.8. However, phosphorylated (urea phosphate) cotton can be distinguished from APO-treated fabric by the following test (*4*): A small piece of fabric from which any wax finish has been removed by solvent extraction is spotted with ammonium molybdate solution. Phosphorylated cotton will immediately turn yellow; APO-THPC–treated cotton does not.

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