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# A Study of the Limiting Oxygen Index of Cotton Samples Treated with Titanium Tetrachloride and Antimony Oxide

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# A STUDY OF THE LIMITING OXYGEN INDEX OF COTTON SAMPLES TREATED WITH TITANIUM TETRACHLORIDE AND ANTIMONY OXIDE

*by A. D. ROBERTSON and N. J. J. VAN RENSBURG*

## ABSTRACT

*The limiting oxygen index values of cotton fabrics which had been treated with various reagents were determined. Antimony oxide did not significantly affect the LOI value of cotton. Titanium tetrachloride increased the LOI value to some extent, but the most significant increase was found when using a combination of titanium tetrachloride and antimony oxide. Titanium tetrachloride and antimony oxide produced fabrics having LOI values significantly higher than those obtained with a commercially available phosphorous-containing flame-retardant.*

## KEY WORDS

Cotton – flame-retardant – titanium tetrachloride – antimony oxide – aminoplast resin – phosphonopropionamide – limiting oxygen index.

## INTRODUCTION

The measurement of the relative flammabilities of polymers is a difficult task. Flammability is normally determined by "rate" or "limit" measuring techniques[1]. Rate measurements are usually cumbersome and require carefully defined and controlled conditions. Limit measurements, on the other hand, are particularly suited to measuring polymer flammability. Fenimore and Martin[2] devised the oxygen index test method, which is based on this principle. The oxygen index test method is simple and is used extensively in flammability studies. In this test a mixture of oxygen and nitrogen is passed up through a cylinder containing the sample which is supported in a vertical position. The partial pressure of the gases is varied to give different mixtures. The minimum percentage of oxygen in the mixture in which a sample will just sustain burning is determined, and this percentage is defined as the limiting oxygen index (LOI) value of the sample. Higher LOI values are indicative of reduced flammability.

The LOI test was originally designed for use with plastic specimens, but there has been a growing interest in the use of this technique to measure the flammability

of textiles[3]. Tesoro and co-workers[4, 5] studied LOI relationships and found that the LOI values of textile fabrics were governed primarily by the chemical composition, with only a relatively small effect attributable to the mass and construction of the fabric. LOI values[1, 3] of various polymers are given below –

| | | |
|---|---|---|
| Polypropylene | : | 0,175 |
| Nylon | : | 0,210 |
| Cotton | : | 0,186 |
| Polyester | : | 0,190 |
| Wool | : | 0,252 |
| Polybenzimidazole | : | 0,406 |
| Polyvinylchloride | : | 0,470 |
| Carbon electrode | : | 0,635 |
| Teflon | : | 0,950 |

Polymers containing halogens or little or no hydrogen are among the least flammable. The LOI values of most of the polymers employed in the textile industry are, however, relatively low. The LOI value of chemically treated textile fabrics was shown to be a linear function of chemical add-on in many cases[5]. In the case of cotton fabrics treated with phosphorous-containing flame-retardants the LOI value was found to be a linear function of the phosphorous content of the fabric[6]. Furthermore, it was reported that several phosphorous-containing flame-retardants of widely varying chemical structure and molecular weight yielded essentially identical LOI values, when added to cotton in such a way that all the fabrics contained the same percentage of phosphorous. Whereas untreated cotton has an LOI value of about 0,180, it was shown that cotton treated to be self-extinguishing in the vertical flame-test had an LOI value of about 0,270.

The LOI value of cotton fabrics which had been treated with phosphorous-containing flame-retardants was studied in great detail by several research workers[6, 7]. In the present report the LOI values of cotton fabrics treated with titanium tetrachloride and antimony oxide are given and compared with the LOI values of cotton fabric treated with a commercially available phosphorous-containing flame-retardant.

## EXPERIMENTAL

A plain weave cotton fabric with a density of 180 g/m$^2$ was used in this study. In some of the durability studies a plain weave cotton fabric with a density of 140 g/m$^2$ was also used. The fabrics were given an alkaline scour prior to the flame-retarding treatments. The flame-retarding composition containing titanium tetrachloride and antimony oxide described in a patent of the National Lead Company[8], was used for the treatment of the fabrics. Solutions containing various concentrations of titanium tetrachloride and antimony oxide were prepared and the cotton fabrics were treated with these solutions as described in an earlier report[9]. In the cases where the effect of titanium tetrachloride on the LOI value of

cotton was studied, the antimony oxide was omitted from the solutions. To study the effect of antimony oxide on the LOI value of the cotton, the samples were treated with various solutions of antimony oxide in 25% (mass/volume) HCl. This was done because the antimony oxide did not dissolve in the above mentioned solutions in the absence of titanium tetrachloride. To study the effect of water soluble antimony-containing compounds on the LOI value of cotton some fabrics were treated with aqueous solutions of potassium antimonyl tartrate. Finally some cotton fabrics were treated with a commercially available phosphonopropionamide flame-retardant.

The durability of the treatments to washing was studied by washing the fabrics in an automatic washing machine at 60°C. Each washing cycle lasted 30 minutes, and was followed by three rinses in cold water (the total rinsing time being 30 minutes) and spin drying for 5 minutes. A domestic washing powder recommended for automatic washing machines was used.

The LOI values of the samples were determined according to the method described by Fenimore and Martin[2]. The sample was mounted vertically in a glass chimney with an inner diameter of 75 mm through which the nitrogen-oxygen gas mixture was passed at a rate of between 4 and 6 cm/second. The sample was burned downwards in the rising gas stream.

## RESULTS AND DISCUSSION

In Figure I the LOI values of cotton fabrics treated with various concentrations of phosphonopropionamide and aminoplast resin are given. The results are in agreement with those of other research workers[6]. The LOI value of cotton treated with aminoplast resin only, showed a very slight increase when the percentage resin add-on was increased. The LOI value of cotton treated with the phosphonopropionamide increased more rapidly with increasing levels of add-on than was the case with the aminoplast resin. The phosphorous-containing compound was therefore a more effective flame-retardant than the nitrogen-containing aminoplast resin. Too high a concentration of phosphonopropionamide on the cotton did, however, have an adverse effect on the flame-retardancy of the fabric. Figure I shows that the LOI value of the cotton fabrics decreased when more than 18% of phosphonopropionamide was added to the fabrics. No explanation can be offered for this phenomenon. Willard and Wondra[6] did not observe this phenomenon in their studies which were, however, restricted to relatively low levels of phosphonopropionamide add-on. They did, however, notice a limiting LOI value when tris (aziridinyl) phosphine oxide (APO) was used as the flame-retardant.

Finally it can be seen from Figure I that much higher LOI values could be obtained by using a combination of aminoplast resin and phosphonopropionamide than by using only one of these reagents. This demonstrates the well-known

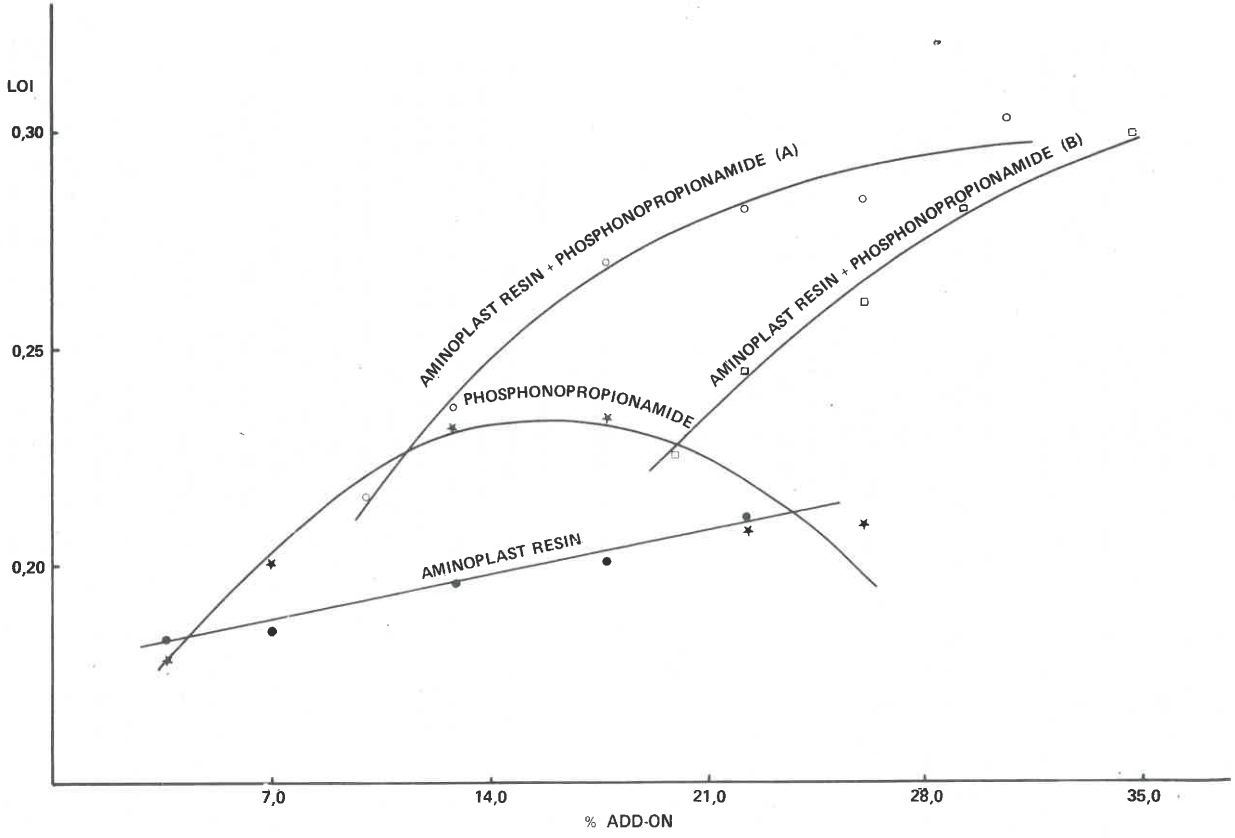


**FIGURE I**

**The LOI values of cotton treated with an aminoplast resin and a phosphonopropionamide flame-retardant at various add-on levels**

synergistic effect between nitrogen and phosphorous containing flame-retardants. The aminoplast add-on level was kept constant (6% in case A and 15% in case B) while the phosphonopropionamide add-on level was increased.

In Figure II the LOI values of cotton fabrics treated with various concentrations of titanium tetrachloride and antimony oxide are given. For purposes of comparison the LOI values of cotton treated with the aminoplast resin (6% add-on) and various concentrations of the phosphonopropionamide flame-retardant are also given. Figure II shows that the treatment of cotton with solutions of antimony oxide in 25% HCl did not affect the LOI value significantly. This is in agreement with the results obtained by several authors, who showed that antimony oxide by itself was ineffective as a flame-retardant[10]. Figure II shows, however, that potassium antimonyl tartrate increased the LOI value of cotton significantly. This effect was, unfortunately, not resistant to washing and this treatment was therefore not further investigated. Figure II furthermore shows that titanium tetrachloride also increased the LOI value of the cotton. The most significant increase in the LOI value of the cotton was, however, obtained when cotton was treated with a combination of titanium tetrachloride and antimony oxide. It is clear from Figure II that a synergistic effect was obtained when titanium tetrachloride was used together with antimony oxide for the flame-retarding treatment. In the case shown in Figure II the ratio of titanium tetrachloride to antimony oxide was kept constant while the percentage add-on was increased. Figure II shows that the LOI values of samples treated with titanium tetrachloride and antimony oxide increased with increasing levels of chemical add-on. The rate of increase in LOI value was greater at lower levels of chemical add-on. Furthermore the results show that, for the same percentage add-on, titanium tetrachloride and antimony oxide produced fabrics with significantly higher LOI values than those obtained with the aminoplast resin and phosphonopropionamide flame-retardant. The difference between the LOI values of the fabrics treated with the two different flame-retardants increased as the percentage add-on was increased, from about 0,06 LOI units at an add-on level of 5%, to about 0,09 units at an add-on level of 25%. Cotton fabrics with an LOI value of more than 0,270 are generally considered to be self-extinguishing in the vertical flame-test. Figure II shows that an add-on level of about 19% aminoplast resin and phosphonopropionamide was required to produce an LOI value of 0,270, whilst an add-on level of only 9,5% was required in the case of titanium tetrachloride and antimony oxide.

Figure III shows the effect of repeated washing on the LOI values of flame-retardant cotton fabrics. Fabrics treated with titanium tetrachloride and antimony oxide showed larger decreases in LOI values upon washing than did fabrics treated with the aminoplast resin and phosphonopropionamide. For similar levels of chemical add-on the LOI values of fabrics treated with titanium tetrachloride and antimony oxide were approximately the same as those of the aminoplast resin and phosphonopropionamide treated fabrics after washing for 25 hours. Figure III also

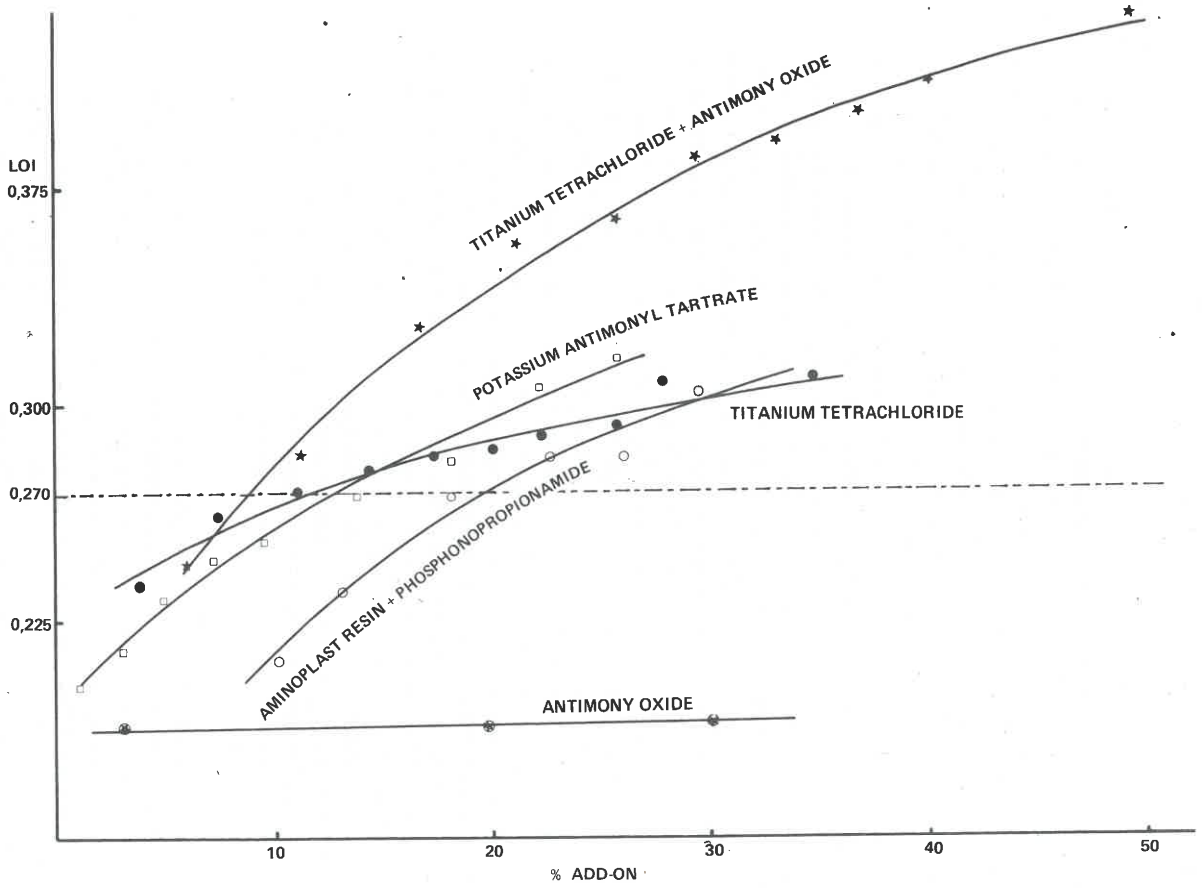


**FIGURE II**

**The LOI values of cotton treated with titanium, antimony and phosphorous containing flame-retardants at various add-on levels**

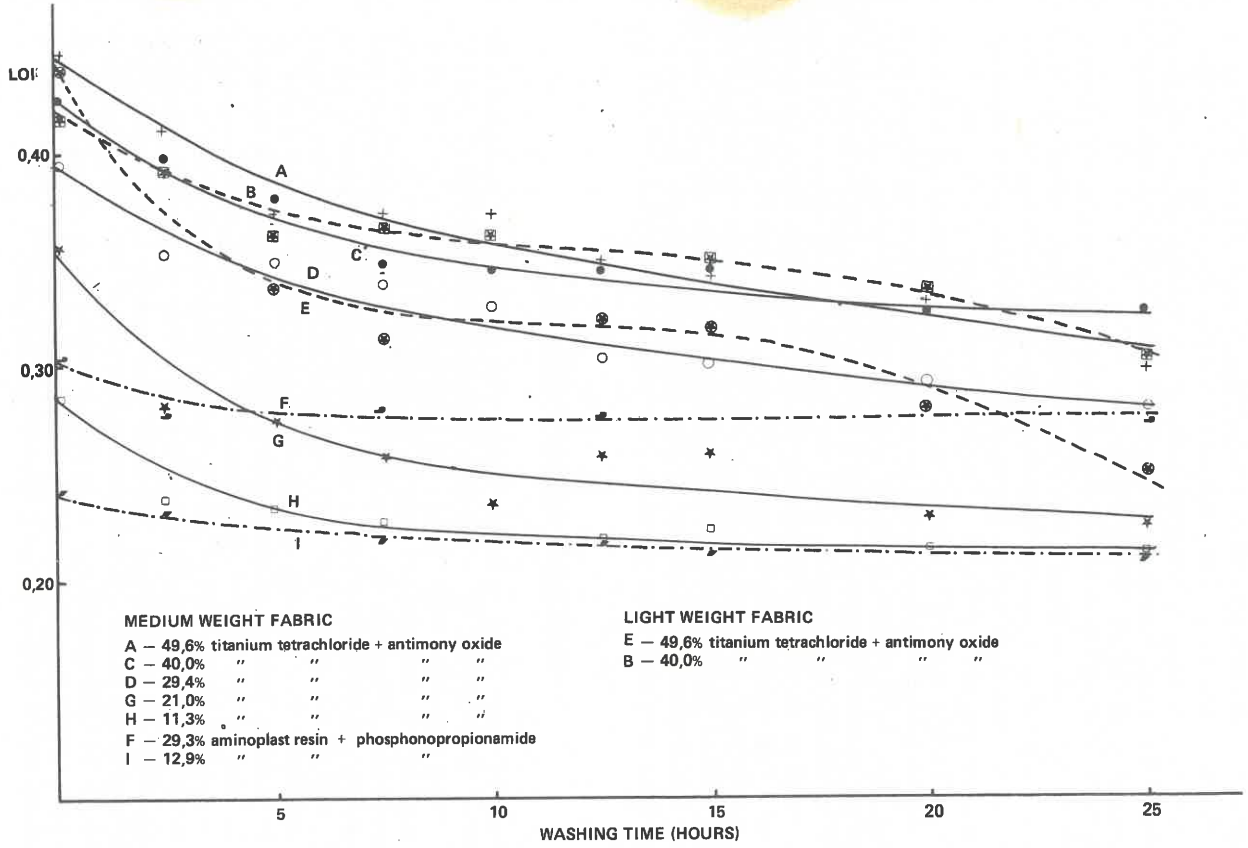


**FIGURE III**

**The effect of washing on the LOI values of cotton treated with various flame-retardants**

shows that, after washing for approximately 20 hours, fabrics which had received a very high level of titanium tetrachloride and antimony oxide add-on (49,6%), had lower LOI values than fabrics which had received lower levels of chemical add-on. This effect was even more pronounced in the case of the lightweight fabrics and was probably due to the degradation of the cotton caused by the high concentration of acid present in the flame-retarding solution.

Figure IV shows the effect of the level of titanium tetrachloride and antimony oxide add-on on the LOI values of cotton fabrics which had been washed for 10 and 25 hours, respectively. A durable flame-retardant finish must pass the vertical flame-test after having been washed for 50 cycles of 12 minutes each, as described under "washing procedure 6,2 (III), in AATCC Test Method 124 – 1969". This gives a total washing time of 10 hours. The washing machine specified in the test method was not available in South Africa and consequently a washing machine with a washing cycle of 30 minutes was used. Assuming that 20 washing cycles in the local washing machine was equal to 50 washing cycles in the machine described in the AATCC Test Method, it can be seen from Figure IV that an add-on level of ca. 20% (or more) of the flame-retardant was sufficient to produce fabrics with LOI values higher than 0,270 after washing for 10 hours. These fabrics would probably pass the vertical flame-test after being washed for 10 hours. It can also be seen that an add-on level of 30% (or more) of the flame-retardant was required to produce fabrics with LOI values higher than 0,270 after washing for 25 hours. These fabrics would probably pass the vertical flame-test even after being washed for 25 hours at 60°C.

## SUMMARY AND CONCLUSIONS

The LOI values of cotton fabrics treated with various flame-retardants were determined. The treatment of cotton with antimony oxide dissolved in 25% HCl did not have a significant effect on the LOI value of the sample. The LOI value could, however, be increased by the use of aqueous solutions of potassium antimonyl tartrate. This effect was unfortunately not fast to washing. It was furthermore found that the treatment of cotton with titanium tetrachloride alone increased the LOI value of the sample. The most significant effect, however, was obtained when a combination of titanium tetrachloride and antimony oxide was used. A synergistic reaction probably occurred when titanium tetrachloride and antimony oxide were used for the flame-retarding treatment of the cotton. It was found that for the same level of chemical add-on, titanium tetrachloride and antimony oxide produced fabrics with significantly higher LOI values than those obtained with an aminoplast resin and phosphonopropionamide flame-retardant. To obtain fabrics with LOI values higher than 0,270, which is normally considered to be the minimum for a fabric to be self-extinguishing in the vertical flame-test, an add-on of 19% of the phosphorous-containing flame-retardant was required, whilst an add-on of only 9,5% titanium tetrachloride and antimony oxide was sufficient.

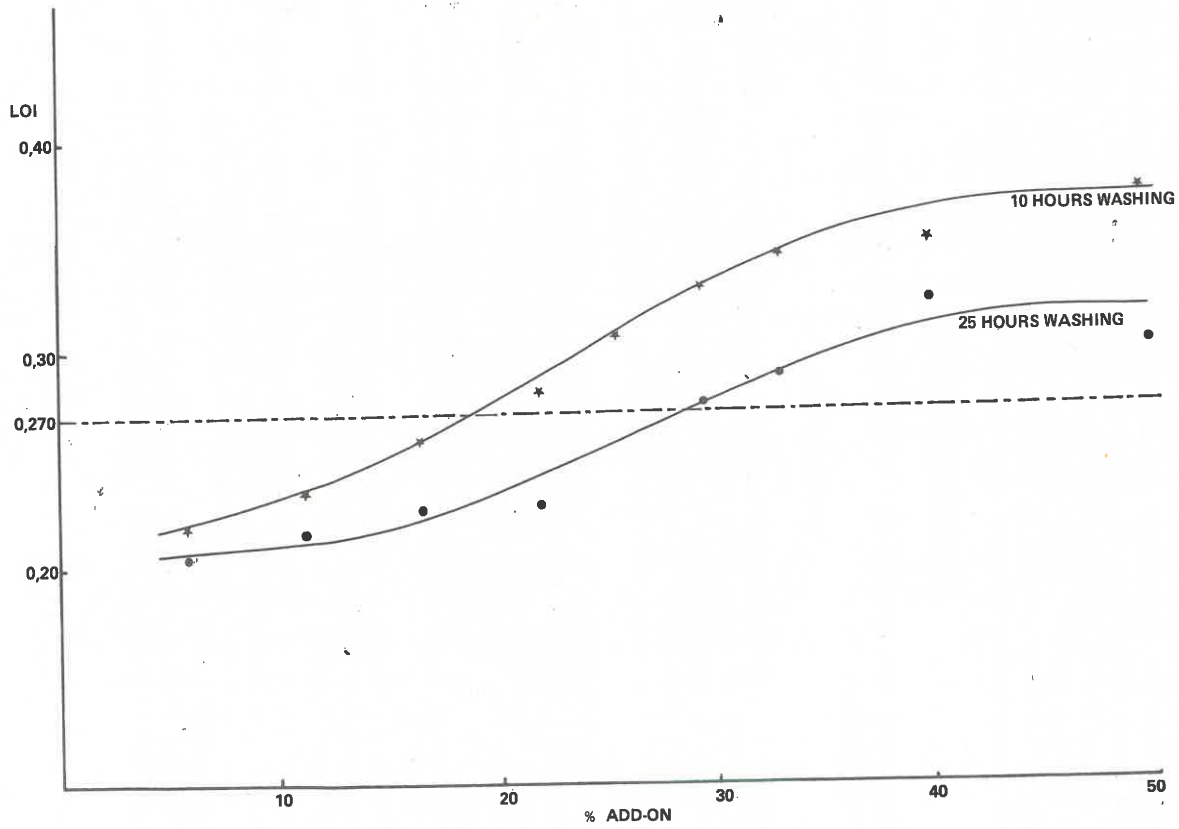


FIGURE IV

The effect of the level of titanium tetrachloride and antimony oxide add-on on the LOI values of cotton fabrics after washing for 10 and 25 hours, respectively

Fabrics treated with titanium tetrachloride and antimony oxide showed bigger decreases in LOI values upon washing, than did fabrics treated with the phosphorous-containing flame-retardant. In spite of this decrease the fabrics treated with titanium tetrachloride and antimony oxide had approximately the same LOI values after washing for 25 hours at 60°C as fabrics treated with the phosphorous-containing flame-retardant (for the same add-on level). An add-on level of 20% titanium tetrachloride and antimony oxide produced fabrics with an LOI value of 0,270 after washing for 10 hours, while an add-on level of 30% was required to produce fabrics having an LOI value of 0,270 after washing for 25 hours.

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