ENVIRONMENTAL
TECHNOLOGY
BEST PRACTICE
PROGRAMME

OPTIMISED PROCESS REDUCES FORMALDEHYDE EMISSIONS

A DEVELOPMENT PROJECT ON COTTON TEXTILE FINISHING

FP70
FINAL RESULTS

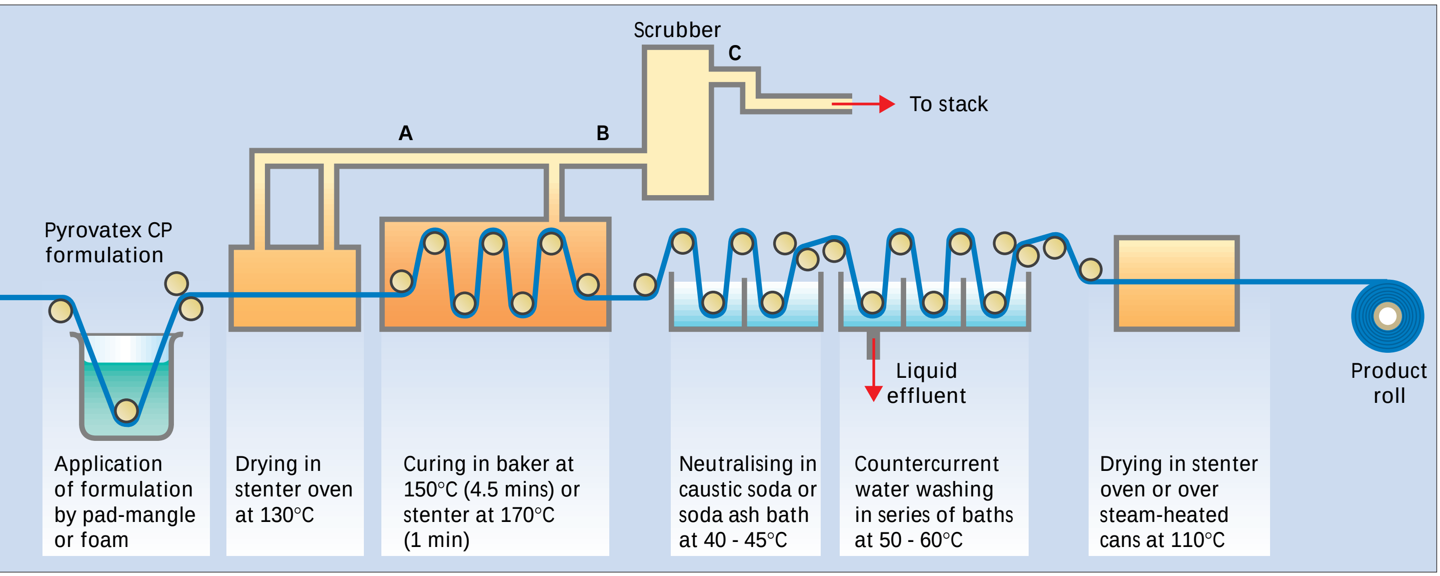
The primary aim of this project was to reduce the formaldehyde emissions released during the application of a flame retardant finish to fabrics.

Applying a flame retardant finish to cotton fabrics can release the volatile organic compounds, formaldehyde and methanol. This project examined alternative formulations to find an optimum recipe that gives the least emissions of these compounds for a satisfactory fabric finish. Process optimisation software helped evaluate the critical elements of the application recipe in a cost-effective manner, and the process performance predicted by pilot-scale work has been confirmed at three textile finishing sites.

The project identified opportunities for other users of flame retardant finishes to:

- **Reduce formaldehyde emissions by up to 75%**
- **Reduce phosphorus levels in effluent**
- **Reduce costs by improving application to fabric**
- **Apply the approach to any operation requiring recipe or process optimisation**

Fig 1 The Pyrovatex CP application process



Background

Conventional cotton-based fabrics are inherently flammable but can be made flame retardant by chemical treatment. For many applications the preferred treatment method involves the application of a reactive finish, which is bonded to the fabric and forms a durable finish.

Pyrovatex CP[1] (developed by Ciba Dyes and Chemicals) is a flame retardant finish for cellulose fibre (eg cotton) alone and in its blends with low synthetic fibre content. The finish is usually applied to the fabric after the colouring stage. The high durability of the finish makes treated fabric ideal for curtains, upholstery, bed linen and protective clothing. The basic application process involves several stages which are outlined in Fig 1.

Pyrovatex CP is an organophosphorus compound which is applied in a formulation that includes a phosphorus-based catalyst and a melamine resin. Under acidic conditions, the Pyrovatex CP bonds directly to the fabric, and the resin also acts as a chemical bridge which improves the bonding of the flame retardant molecule to the fabric (Fig 2). In addition to these principal reactions, side reactions can occur during the high temperature stenter and curing stages, leading to the formation of formaldehyde (Fig 3). Methanol is also formed, adding to the volatile organic compounds (VOCs) in the exhaust gases. During the final neutralising and washing stages, phosphorus is transferred into the wash water, adding to the cost of processing effluent.

Fig 2 Chemistry of the Pyrovatex CP system

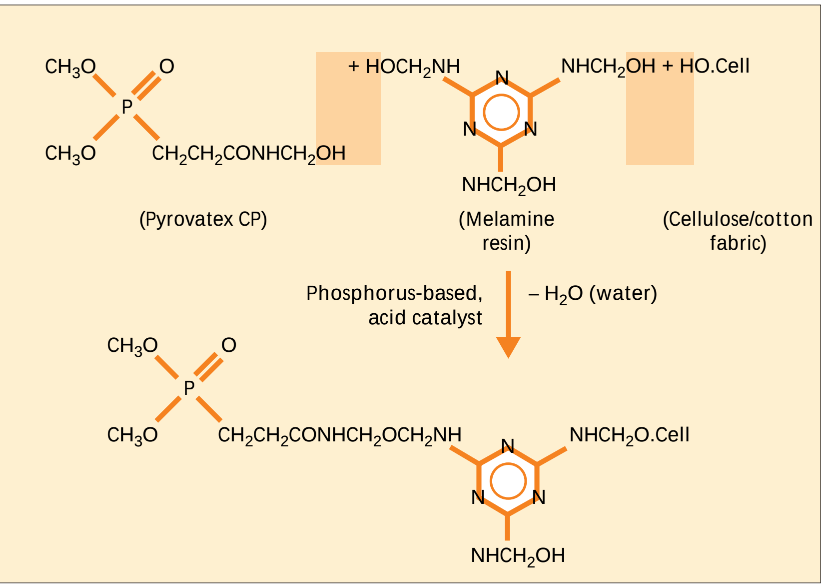
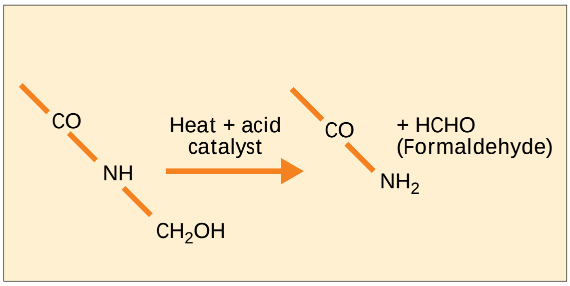


Fig 3 Formation of formaldehyde



To comply with the Environmental Protection Act 1990, emissions from processes for applying flame retardant finishes must not exceed the limits specified in the *Secretary of State's Process Guidance Note PG6/8*. As formaldehyde emissions cannot be controlled by good housekeeping measures alone, the application process needs to be optimised to minimise its environmental impact while still producing fabric with satisfactory flame retardant properties.

This project was funded by the Department of the Environment under the Environmental Technology Innovation Scheme (ETIS). The Scheme, which is now closed, provided grant assistance for pre-competitive industrial research in the environmental field and has been superseded by the Future Practice element of the Environmental Technology Best Practice Programme. More information can be obtained from the Environmental Helpline on 0800 585794.

Project Aims

The main aim of this project was to reduce emissions of formaldehyde during the application of Pyrovatex CP to a target level of 5 ppm – well below the current formaldehyde limit of 20 ppm set in PG6/8 – while maintaining fabric qualities.

[1] Pyrovatex CP is a registered trademark of Ciba Specialty Chemicals

Secondary aims were to reduce the level of phosphorus in liquid effluent and to obtain a greater understanding of the influence of each process variable on the production of VOCs.

Project Approach

At the start of the project, each part of the Pyrovatex CP application process was assessed to gauge its impact on formaldehyde emissions.

Early results indicated that the application recipe variables significantly influenced emissions, and so studies were focused on the recipe components and their relative and absolute concentrations.

Development of analytical methods

To ensure accurate, real-time measurement of formaldehyde in the gaseous effluent, a novel monitoring technique was developed using a gas cell in a Fourier transform infrared (FTIR) spectrometer. The equipment enabled on-line samples to be collected and maintained at process temperature while spectra were recorded. Wet chemical methods were also used to analyse certain samples to verify the results. Results were shown to be accurate to ±0.5% ppm. Total VOC emissions were measured using a flame ionisation detector. Samples for both measurements were taken at the same time from vent gases after the drying and curing stages and after the scrubber (points A, B and C respectively on Fig 1).

Optimising the application recipe

As well as minimising formaldehyde emissions, the application recipe has to result in a fabric with satisfactory flame retardant properties. The aim was to produce a fabric with a limiting oxygen index (LOI, a measure of the flame retardancy – as a percentage – of oxygen needed to sustain combustion of the fabric) of over 28. At the same time the target was to develop a recipe which resulted in formaldehyde emissions of under 5 ppm.

The current Pyrovatex CP application recipe has five components: Pyrovatex CP; catalyst; resin; softener; and wetting agent. To suit a particular process or fabric application, the component concentrations used can vary slightly from site to site. For this project, a ‘standard’ recipe was used as control in the pilot-scale trials. Emission levels and fabric properties for each test run were compared with results from this recipe. The standard recipe is shown in Table 1.

To enable the recipe to be optimised, the impact of each component, with regard to its relative and absolute concentrations, needed to be evaluated. In addition to the components in the standard recipe, eight other resins and seven catalysts were also considered.

A sophisticated process optimisation software package was used to reduce the number of experiments needed to arrive at the optimum recipe while minimising formaldehyde emissions. The software allowed the effect of each component on flame retardancy to be identified. As a result it was possible to identify an optimum recipe through statistical analysis and ongoing modification.

Table 1 Pyrovatex CP application recipe and pilot-scale results

	Standard recipe	Optimised recipe
Recipe component (g/litre)		
Pyrovatex CP	280	260
Melamine resin	35	32
Softener	25	27
Acid catalyst	20	15
Wetting agent	1.25	1.25
Fabric response (%)		
LOI	28	30
Phosphorus on fabric	1.9	2.0
Emission level after curing stage (ppm)		
Formaldehyde	20	5

Project Results

Pilot-scale results

Pilot-scale results with different resins and catalysts showed that the components used in the standard recipe gave the best results with regard to LOI, formaldehyde emissions and level of Pyrovatex CP fixation (measured by the percentage of phosphorus retained on the fabric after treatment). The optimised recipe concentrations using these components are shown in Table 1. Although the changes to the standard recipe are small, the optimised recipe reduces formaldehyde emissions by 75%, and improves both LOI and fixation level.

Industrial trials

The optimised recipe was used at three textile finishing sites to verify that the pilot-scale results could be achieved in industry. All three sites used typical textile finishing equipment (Fig 1), with two using pad-mangles to apply the Pyrovatex CP application recipe, and one using foam application. The test runs involved treating a minimum of 1 000 m of fabric. Formaldehyde emissions were measured in the combined vent gases after the stenter/curing stage (point B on Fig 1) and showed significant reductions (Table 2). A reduction in the amount of phosphorus in the liquid effluent was also noted, due to the reduction in phosphorus-based catalyst in the new recipe and increased fixation of Pyrovatex CP to the fabric. (All fabric treated during the trials complied with quality specifications and was subsequently sold.)

Table 2 Industrial trial results

Site	Standard recipe formaldehyde emissions (ppm)	Optimised recipe formaldehyde emissions (ppm)	Reduction (%)
1	11	4.5	59
2	7	4.5	36
3	4.3	2.5	42

Further results

- Liquid effluent reduction

  Pilot-scale trials with alternative catalysts showed that using diammonium hydrogen phosphate as the catalyst and ammonium hydroxide in the neutralising bath enables the catalyst to be regenerated and the wash liquor to be recycled, ie mixed with a reduced amount of 'fresh' catalyst on each subsequent run. As well as greatly reducing effluent discharges and raw material use, the modified recipe with recycled effluent produced fabric with a higher LOI and fixation level than that resulting from the standard recipe. This modified application recipe has yet to be tested at an industrial site.

- Total VOC emissions

  Although formaldehyde emissions were reduced during the project, other organic emissions remained significant. Further work, beyond the scope of this project, would be required to reduce these emissions at source, although they fall within current emission limits.

Project Benefits to Users of Flame Retardant Finishes

- Using a process optimisation software package significantly reduced the number of experiments needed to optimise the Pyrovatex CP application recipe. This was the key factor in the success of the project. The emission levels and fabric properties predicted by the software were achieved in pilot-scale trials.
- Optimisation of the recipe can cut formaldehyde emissions by 75% (in pilot-scale trials) and typically by 50% in industrial trials. The smaller reduction seen in industry may be due to some cross-contamination from previous fabric runs.
- Optimising the recipe can reduce phosphorus levels in liquid effluent by up to 50%. The optimised recipe uses less phosphorus-based catalyst and also results in more phosphorus being fixed to the treated fabric.
- VOC emissions can be reduced with just a small adjustment to the application recipe - no process changes were required in this study. Overall, the optimised recipe uses less raw material to achieve the same fabric response and this is likely to save costs when applied on an industrial scale.
- Results from the industrial trials suggest extended trials in the textile finishing sector may be justified. If successful, the optimised recipe may be adopted throughout the industry. Pilot-scale work revealed potential to significantly reduce the amount and cost of liquid effluent from the Pyrovatex CP application process, though this approach still has to be proved in industry.

Additional Benefits

The optimisation procedures used in this project may be applied to many other process optimisation problems. In particular, they could be used for other formaldehyde-based resin application processes in the textile finishing sector, cutting emissions and improving environmental performance. The approach is also applicable to other industrial sectors, using similar processes, such as fibre and compressed board manufacturers, and surface laminating industries.

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