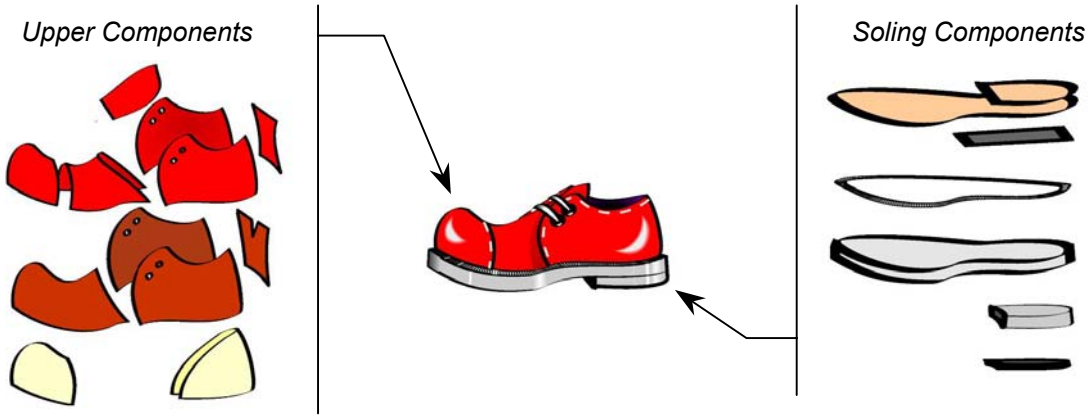
BONDING OPERATIONS FREE OF HAZARDOUS SOLVENTS IN THE COMPLETE PROCESS OF FOOTWEAR MANUFACTURING (CALSINDIS)

LIFE02 ENV/E/00242 PROJECT

1. Background

A shoe is comprised of several components that must be assembled. These components are made up of different materials, with diverse physical and chemical properties. Traditionally, these components were assembled through stitching. In the 50's, adhesives appeared and their increasing use in shoe production enabled the mechanisation of processes, a reduction in times and even the production of creative models or new materials that could not be assembled through stitching.



At present, the adhesives most frequently used in the footwear industry are polyurethane and polychloroprene adhesives based on organic solvents. Despite the advantages of these adhesives, their use entails some risks such as environmental impact and harmful effects for the human body. The most important disadvantages of these adhesives are related to hazardous organic solvents, mainly *n*-hexane, which causes a polyneuropathy. This has caused significant alarm among the population.

This polyneuropathy is an illness related to work activities and characterised by a progressive lose of limbs' force. Among the factors contributing to the appearance of this illness, there is the absence of protective devices in the work place, neither individual (masks, gloves, etc.) nor collective (extraction booths), as well as high temperatures in the work environment, bad ventilation, and maybe, too many emission focuses of hazardous organic solvents.

Due to the alarm caused among the population, last 26th September 1998, the Chamber of Deputies (lower Chamber of Spanish Parliament) approved a Proposal that urged the authorities to boost the use of adhesives with reduced effects on the footwear industry workers' health.

Nevertheless, the use of organic solvent-based adhesives is harmful for human health and it also causes environmental impact. Volatile Organic Compounds (VOCs) present in the atmosphere contribute to the formation of polluting smog, and some of them come

from emissions of organic solvents to the environment by certain industrial activities.

Therefore, the Community environmental regulations foresee a short-term reduction in the use of organic solvents employed in footwear industry. Consequently, a Directive of the European Union Council (1999/13/CE) concerning the restriction of volatile organic compound emissions caused by the use of volatile organic solvents in certain industrial activities was enacted. This Directive was incorporated to the internal legal system by the Royal Decree 117/2003 of 31st January 2003. This Directive covers a reduction of organic solvents up to 25 g/pair of shoes and its application will be mandatory for the footwear industry in the year 2007.

On the other hand, in June 1999, the European Council draw some conclusions on which the European Commission based the preparation of a proposal for the regulation of hazardous substances and chemicals, whose main objective is achieving sustainable development (*COM (2003) 644 final. Proposal for the Registrations, Evaluations, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency and amending Directive 1999/45/CE and Regulation (CE) on Persistent Organic Pollutants*). In accordance with this proposal, both the producers of chemicals (in this case adhesive producers) and the industrial users (footwear manufacturers) will be obliged to assess the safety of their products concerning the part of the product life cycle they participate in (concerning all those uses that are not covered by the previous actors in the supply chain), and including the withdrawal and management of waste. Therefore, this new Community policy will affect directly the footwear and related industries. This proposal will be approved by the European Parliament and the European Council of Ministers, and its implementation is foreseen for the period 2005-2006.

Furthermore, the award of the European Ecological Label for footwear limits the use of organic solvents in adhesives and finishing products (for further information go to www.ecoshoe.info). Although footwear producers can voluntarily apply for the award of this label, its obtaining would enhance competitivity of footwear when exported to countries with a very restrictive environmental policy.

Considering this, as well as the need to fulfil a large list of European Directives regarding environmental protection and health at work, the current tendency of the footwear industry is aiming at the elimination or substitution of organic solvent-based adhesives in a near future.

2. Project approach

At present, with regards to certain operations, there are some alternatives available to the use of solvent-based adhesives and surface treatments. Nevertheless, manufacturers usually ignore that they exist or they refuse their use, maybe due to lack of information.

Within this context, the European Commission approved the **"Bonding Operations Free of Hazardous Solvents in the complete Process of Footwear Manufacturing (CALSINDIS)"** project within the *LIFE-Environment Programme*.

The main objective of this project is to provide the footwear industries with a bonding technology alternative to the use of solvent-based adhesives and surface treatments, through the use of other products that are less harmful for the human body and for the environment, thus assuring the quality of the final product and carrying out a wide dissemination of these alternatives among the companies in this sector.
The Technological Institute for Footwear and Related Industries, INESCOP, participates in this project as co-ordinator and responsible for its execution against the European Commission, for its dissemination, and for the carrying out of different laboratory analysis on alternative adhesives and quality tests on footwear produced with these adhesives.

A footwear manufacturing company called PIKOLINO'S supplied the footwear components needed to carry out the tests on adhesives for each manufacturing operation and they are currently implementing production lines where only solvent-free adhesives are used.

COMPOSAN, producer of adhesives for the footwear industry, participates in the project supplying and adapting different adhesives, which are free of organic solvents, in order to carry out the laboratory tests and factory trials.

VOCs emissions to the atmosphere will be considerably reduced, through the elimination of solvents in footwear bonding operations, thus contributing to the fulfilment of several European Directives with regards to health at work and the environment.

3. Project Development

This project started in October 2002 and, the adaptation of a production line, where only solvent-free adhesives are used, was carried out in PIKOLINO'S by February 2004. Currently, this adaptation is being extended to other production lines in PIKOLINO'S.

First of all, aiming at achieving the project objectives, several alternative adhesives available on the market were considered. Most of these adhesives are currently used in other industrial sectors:

a) Solvent-based adhesives, in which current solvents, mainly *n*-hexane, are replaced with other less harmful solvents.

This is the first alternative that emerged from the first people affected by polyneuropathy illness caused by *n*-hexane. These are some adhesives such as glue or cement (natural rubber in organic solvent solutions) frequently used in the preparation of footwear uppers (stitching, etc), in which *n*-hexane has been replaced with other solvents or solvent mixtures that are less harmful for the human health.

The properties of these adhesives make them suitable for being used in footwear production. Nevertheless, the use of this adhesives somehow solve problems related to the health of workers, but the emission of VOCs to the atmosphere is not reduced. For this reason, and considering that other more suitable options have been found, the use of this adhesive has not been proposed as an alternative to the adhesives traditionally used in the footwear upper preparation operations.

b) Water-based adhesives

These adhesives are considered to be the most appropriate for the aim of this project, as they are the most important alternative to solvent-based adhesives. They are used in different bonding operations: preparation of uppers (stitching, lining preparation, etc.), placing of insocks as well as in upper-sole bonding, one of the most important operations in footwear manufacture.

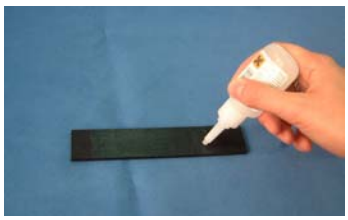
c) Solid adhesives (hot-melt)

In the footwear industry these adhesives are used for toecaps and stiffeners, in the lasting operation as well as in the upper-sole bonding operation.

At present, there are different solid adhesives for upper-sole bonding and these are an alternative in order to substitute the traditional solvent-based adhesives in the production of some types of footwear.

As a result of the project, a new adhesive that is proposed as an alternative for thermoformed insoles bonding is proposed.

d) Reactive adhesives



The use of polyurethane reactive adhesives, vinyl adhesives that can be reactivated through UV radiation as well as cyanoacrylate adhesives has been considered.

Although some of these adhesives have proved to produce strong joints, they generally show a lack of tack needed for bonding the sole to the lasted upper. For this reason, their use is not proposed for this kind of application.

The properties of adhesives have been characterised through different techniques aiming at establishing their suitability for the manufacturing of footwear:

Infrared spectroscopy: this allows to determine the chemical structure of the base polymer of the selected adhesives, as well as any variation in their formulation.

Measurement of particle size of adhesives in aqueous dispersion. The distribution and mean size of particles is related to the dispersion stability against sedimentation, and to their easy penetration in porous materials or their capacity for film formation.

Solid content in water-based adhesives. This test allows the determination of solid content in adhesives, through the difference in weight after the complete evaporation of water. The greater the solid content in an adhesive is, the greater its performance. Therefore, a smaller amount of adhesive should be applied on materials to bond. This has been considered for the implementation of alternative adhesives in the manufacturing process, as in general the solid content in water-based dispersion adhesives is greater than in traditional solvent-based adhesives. Therefore, nowadays workers apply smaller quantities of adhesive, although they were used to applying larger quantities when they worked with traditional adhesives.

Grammage. This test is related to the solid content and it allows to determine the weight of the adhesive film applied to the substrate.

pH. The maintaining of pH conditions is very important in the case of water-based adhesives, as a variation of the pH means the adhesive destabilization.

Brookfield Viscosity, this is one of the properties that determines the spreadability of the water-based adhesive.

Controlled stress rheometry, for measuring the viscosity in molten state. This allows the determination of the rheological behaviour of the adhesive film at different temperatures after the elimination of water. This also allows to determine the rheological properties of hot-melt adhesives.

Study on the reactivation temperature. Usually polyurethane adhesives loose their tack after the elimination of solvent or water. Due to this specific property, when dried, they must be heat reactivated in order to provide them with the tack needed for bonding. For this reason, it is advisable to carry out a study on the reactivation temperature that is more appropriate for polyurethane water-based dispersions. The reactivation temperature is a critical parameter that must be monitored during the manufacturing process, as in water-based dispersions, the temperature range within which good results are obtained is very narrow.

Adhesive properties. The appropriateness of adhesives for bonding different materials used for footwear manufacture is determined through T-peel strength and shear strength tests.

Considering the results of this characterisation, COMPOSAN made some modifications in the their adhesive formulations, in order to adapt their properties to the bonding conditions and requirements for all the operations of footwear manufacture. These requirements are the following:

- Preparation of uppers: assembling the different pieces that make up the shoe upper, folding, etc. Requirements for these adhesives concerning unsticking of pieces are not too demanding as the pieces are usually stitched after being assembled. Nevertheless, the main properties of these adhesives must be the following:

  - Quick drying
  - Suitable tack, and long open time, as due to organisational reasons in factories, the assembling of pieces is carried out some time after the application of the adhesive.
  - Instant bonding.
  - The adhesive must not stain or harden the surfaces on which it is applied.
  - The adhesive must not cause problems when stitching the pieces as some adhesives may stick to the needle thus hindering the stitching process.

- Lasting operations: this operation consists in positioning the assembled upper and the insole on the last. This assembly is then subjected to stabilisation of the upper through the simultaneous application of temperature and humidity, in order to avoid that leather recovers its two-dimensional shape after last-pulling. Due to this stabilisation process, adhesives used for lasting must present the following characteristics:
  - High crystallisation/cross-linking speed
  - Temperature resistance (T > 120ºC)

- Upper-sole bonding operation: this is one of the most important and critical operations concerning the requirements of this joint and the footwear quality. Adhesives used must fulfil the following requirements:

  - Versatility, as sometimes the bonding is made with very different materials.
  - High crystallisation speed and high initial cohesion in order to prevent the shoe unsticking when removed from the press.
  - Suitable viscosity, so as to make its application and dosage easier.

- Adhesives for insocks must meet the following demands:

  - Quick drying process
  - Long open time and suitable tack
  - Instant bonding
  - They must not stain or harden the insock material
  - They must allow to easy move the insock when placing it

Furthermore, in the upper-sole bonding operation, it is usually needed to carry out a surface treatment on the sole material before applying the adhesive. For instance, *halogenation* (a solvent-based chemical treatment) is usually carried out on vulcanised rubber soles. During this project, the replacement of these surface treatments with any of the following solvent-free alternative products has been considered:

a) Water-based halogenation

b) Treatment with acids, both organic and inorganic. This is a treatment frequently used for the surface treatment of vulcanised rubber in other sectors.

c) UV radiation treatment. This treatment consists in exposing materials to ultraviolet light from mercury lamps connected to the corresponding electronic device and with the appropriate protection devices for the workers and the environment. It has been proved that this technique is the most appropriate for the treatment of sole materials used in footwear manufacture by PIKOLINO'S.

Effectiveness of these treatments has been determined through different experimental techniques:

Infrared spectroscopy, which allows to analyse the chemical modifications caused on materials by the surface treatment.

Measurement of contact angles, aiming at the obtaining of surface energy of materials treated. This property is directly related to the capacity of a material to be bonded with adhesives. A variation in surface energy means a modification in the chemical structure of the surface, thus affecting the adhesive properties.

Realisation of peel strength tests, in order to determine the force needed to unstick the materials previously bonded with the adhesive.

After selecting the most appropriate adhesives for each bonding operation, these have been introduced in the footwear manufacturing line of PIKOLINO'S. Therefore, all solvent-based adhesives traditionally used in footwear manufacture have been replaced by alternative solvent-free adhesives.

On the one hand, some modifications have been needed in the manufacturing line concerning the working procedure, such as the setup of new equipment for the application of water-based adhesives in the preparation of uppers. In this way, the appropriate dosage of the product is assured.

On the other hand, adhesive applying systems have been adapted for the lasting operation, in order to adapt the alternative adhesive developed for this aim during the project.

Concerning the conditions in footwear manufacture, no important modifications have been needed. Only the use of cool ovens after the press in upper-sole bonding is recommended, as well as the use of drying ovens during the lasting operation.

Shoes manufactured under these conditions have been subjected to the usual quality control tests at INESCOP, and it has been proved that both the adhesives selected and the manufacturing conditions are suitable for the production of quality footwear.

With regards to the alternative surface treatments, some technical problems occurred during the development of this project, which have hindered their incorporation in the manufacturing line. Nevertheless, the implementation of the alternative system will not be considered until these technical problems are overcome, after the project completion.

Finally, and concerning the LIFE project specifications, several activities for the dissemination of results have been carried out during the development of the project. This dissemination has been carried out through the attendance to several footwear trade fairs, both at a national and international level, and the publication of some reports in journals and in the INESCOP web site. An informative session related to the project results was held, during which attendees made a visit to a manufacturing line of PIKOLINO'S, where the use of traditional adhesives has been completely replaced by solvent-free adhesives adapted during the project. Furthermore, some tests have been carried out in different footwear manufacturing companies in order to show a demonstration of the use of the different alternative adhesives proposed.

4. Obtained results.

As a result of this project, different alternative solvent-free adhesives have been chosen for every bonding operation in footwear manufacture:

Bonding operation	Traditional adhesive	Alternative adhesive
Preparation of uppers (stitching, lining, folding, etc.)	Adhesives such as glue or cement applied with a brush	Polychloroprene water-based adhesives applied with spray.
		Latex adhesive. Water-based natural rubber applied with spray.
Lasting	Organic solvent-based polychloroprene adhesive applied with a brush or by machine.	Polychloroprene water-based adhesive resistant to temperature, applied with a brush or by machine.
Upper-sole bonding	Organic solvent water-based polychloroprene adhesive applied with a brush.	Polyurethane water-based adhesive, applied with a brush or by machine.
Insert placing	Adhesives such as glue or cement applied with a brush.	Polychloroprene water-based adhesive, applied with a brush.
		Hot-melt adhesive, machine applied.

Water-based adhesives


Hot-melt adhesive

As it has been mentioned before, the adaptation of a manufacturing line has been carried out in PIKOLINO'S, where all traditional solvent-based adhesives have been replaced with the alternative adhesives chosen.

Different women, men and children shoe models have been produced in this manufacturing line.

The usual quality tests have been carried out on these shoes in order to determine the upper-sole bonding strength. The following table shows some of the obtained results:

Type of footwear	Peel strength (N/mm)	Minimum requirement (N/mm)
Town footwear for women (Sandals)	3.8	3.5
Town footwear for women (Ankle boots)	9.3	3.5
Town footwear for women (Knee-high boots)	8.0	3.5
Town footwear for men	8.4	4.5

The results of these tests have proved that, after adapting the manufacturing conditions, peel strength values obtained are higher than the minimum requirements demanded for every type of footwear. Therefore, the appropriateness of adhesives and manufacturing conditions has been proved.

Several wear trials have been carried out with the manufactured shoes, and results are also satisfactory.

As a result of the implementation of the technology proposed in the project, a considerable reduction of the use of solvents in the overall footwear manufacturing process will be achieved, thus providing the following advantages (environmental and others):

- Use of safe and ecological adhesives.
- Reduction of the emission of VOCs to the atmosphere.
- Improved conditions at work.
- Enhanced competitivity of the European footwear industry worldwide.

In Spain, the number of footwear manufacturing companies amounted 2,287 by the year 2003, employing a total of 44,453 workers and producing 171 million of pairs. It is estimated that the implementation of solvent-based adhesives developed in this project in the whole Spanish footwear industry, will reduce the emissions of VOCs to the atmosphere by 3,600 t VOCs/year, with an estimated cost of 157 €/t VOCs, that means, about 565,000 €/year for the Spanish footwear industry. Furthermore, if solvent-based surface treatments were replaced by the treatment proposed in the project, the emissions of VOCs from footwear manufacturing activities would be reduced to 7,200 t VOCs/year.

Consequently, the use of solvent-free adhesives proposed in the project will help both the companies in the footwear sector and other member countries to fulfil the European legislation concerning the protection of the environment, the improvement of health at work and other aspects which could be considered of interest for this industry.

This legislation will affect the footwear industry in the European Union, which is comprised of about 14,000 shoe companies, employing about 300,000 direct workers.