



Adhesión y adhesivos

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SURFACE TREATMENTS USED IN THE FOOTWEAR INDUSTRY

TRADITIONAL METHODS AND CT-100 SURFACE TREATMENT

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I. INTRODUCTION TO THE CT-100 TREATMENT

The objective of the surface treatments is to increase the compatibility between the sole materials and the adhesives.

TREATMENT WITH UV RADIATION (CT-100)

It's an alternative treatment to the traditional methods employed to increase the adhesive properties of the MATERIALS USED IN THE FOOTWEAR INDUSTRY, for bonding with polyurethane adhesives

Advantages

- It physically and chemically modifies the surface of the wide majority of materials used in the footwear industry with positive results (98%).
- It is quick and cheap
- Complicated models (laterals, tongues...) can be treated easily (the UV radiation and the oxidation atmosphere have access to complex geometry)
- It does not show environmental problems
- It works at atmospheric pressure and without chemical agents



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- It allows high production without stocked treated soles, saving money and time.

Halogenation with trichloroisocyanuric acid (TCI):

THE MOST TRADITIONAL TREATMENT USED IN THE FOOTWEAR INDUSTRY

DISADVANTAGES:

- Halogenating solutions are toxic (chlorine vapour emanations are produced)
- Solutions are unstable with time
- Treatment requires relatively long times (6 hours minimum)
- The rubber formulation can affect negatively the halogenation treatment

II. MATERIALS INDEX AND SURFACE TREATMENTS.

COMPARATION BETWEEN TRADITIONAL TREATMENTS AND THE NEW CT-100 TREATMENT

1. TR-Thermoplastic rubber	6
2. Vulcanised rubbers (SBR, NBR, etc...)	10
3. EVA copolymers (microporous)	14

1. THERMOPLASTIC RUBBER-TR

Styrene-butadiene-styrene rubber. They can be transformed by heat and get degraded by solvents contained in the halogenating solution.

Common treatment: Halogenation with trichloroisocyanuric acid (TCI) solutions in estheres and ketones

-Disadvantages:

<Halogenating solutions are toxic

<TCI solution degrades and weakens the TR surface

CT-100 treatment: Direct treatment, without previous steps. Excellent adhesion values are obtained after CT-100 treatment, whether solvent-based adhesive or water-based adhesives are employed, with or without isocyanate (hardener).

Treatment durability with and without adhesive: 1-3 months (See Figures)

Results obtained from commercial formulations tested in laboratory

Occasional incidences:

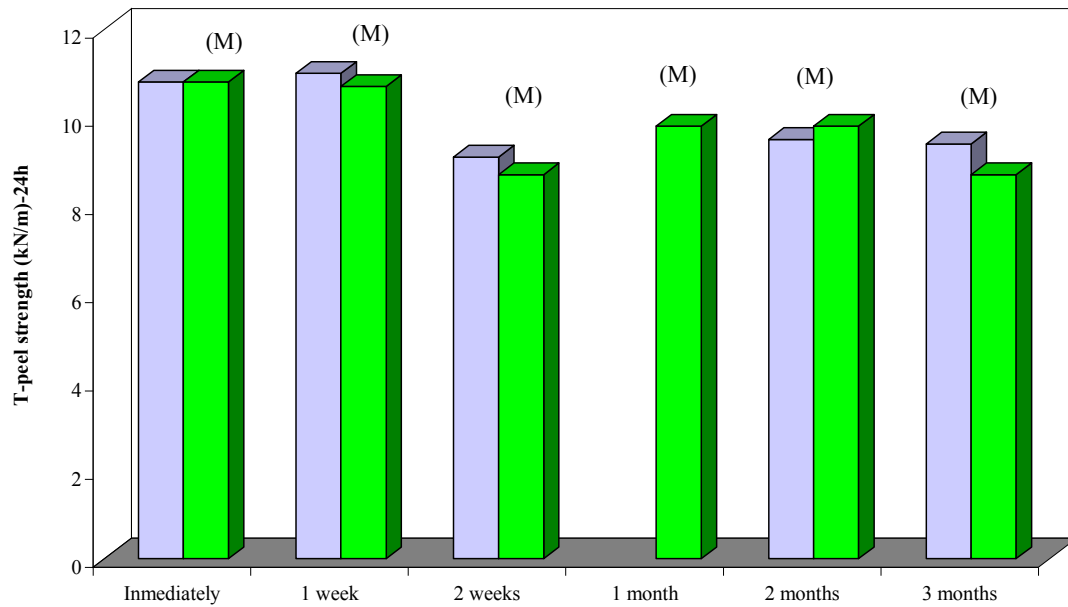
– Silicones can be present on the rubber surface, making it necessary to perform a solvent wiping previously to the CT-100 treatment. Consulting your TR rubber supplier is recommended, because these materials don't need mold releasers.

–White or clear colours require paying especial attention to the reactivation process (60°C as a minimum).

1. THERMOPLASTIC RUBBER-TR

□ With adhesive
■ Without adhesive

TR-Durability of the surface treatment with and without adhesive



M=cohesive failure in the rubber

1. THERMOPLASTIC RUBBER-TR

Durability of the TR rubber treated with CT-100

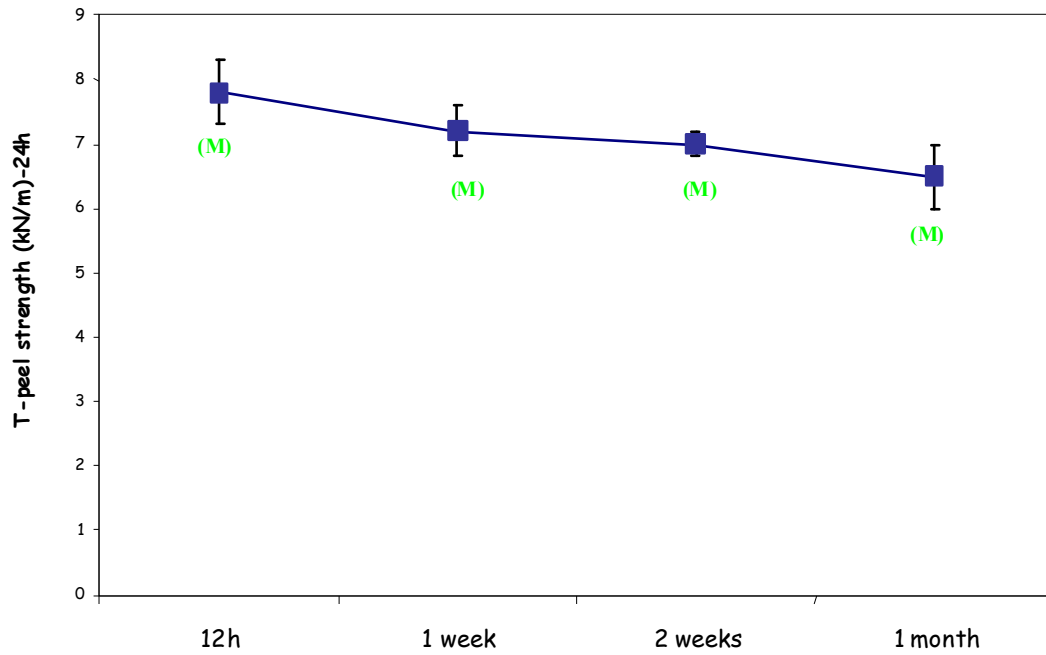


Figure 1

(M)= cohesive failure in the rubber

Sovent based adhesive

1. THERMOPLASTIC RUBBER-TR



Adhesion value= 12.7 kN/m (M)

2. VULCANISED RUBBERS (SBR, NBR, etc...)

Styrene-butadiene-styrene rubber vulcanized using sulphur. These materials contain adhesive compounds in their formulation that can migrate to the surface producing serious adhesion problems. Adhesion is facilitated when the synthetic rubber (SBR) content is high.

Habitual treatment: Surface roughing plus halogenating treatment with trichloroisocyanuric acid (TCI) solutions in estheres and ketones.

-Disadvantages:

<Halogenating solutions are toxic

<Roughing tongues, thin materials.....etc is very difficult and expensive.

<Vulcanized rubbers with surface waxes and high oil content require manual halogenation process with a brush to obtain good adhesion results.

CT-100 treatment: Excellent adhesion results after CT-100 surface treatment with solvent-based polyurethane adhesives or water-based polyurethane adhesives.

– Mechanical roughing is necessary previous to CT-100 surface treatment to remove paraffin wax and zinc stearate from the rubber surface.

–Adding isocyanate to the adhesive is mandatory, to insure good adhesive joints. Depending on the rubber formulation, the initial adhesive strength can be low, however if the CT-100 treatment is correct, the final adhesive strength will be excellent.

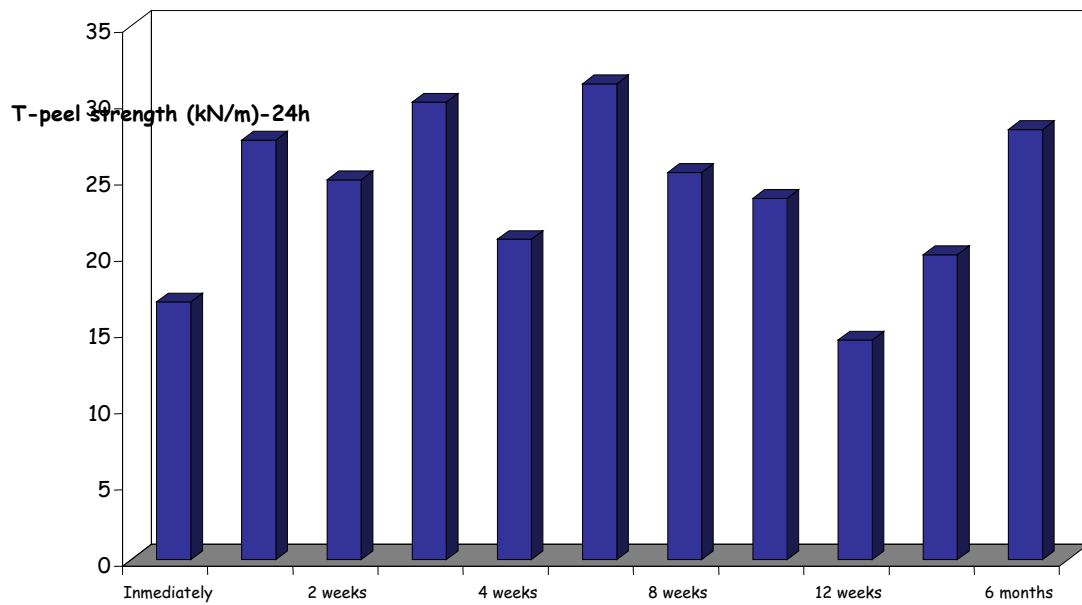
Treatment durability: 2-3 weeks (in general for all kind of rubbers). Some formulations up to 2-3 months.

Results obtained from commercial formulations tested in laboratory

Occasional incidences: Paying attention to all steps of the adhesion bonding formation is necessary: reactivation (70-80°C), pressure, adhesive, isocyanate...

2. VULCANISED RUBBERS (SBR, NBR, etc...)

SBR-Ruiz Alejos-Piles Model (M)/Roughing- CT-100 treatment/PU+5%Desmodur RFE/leather
SURFACE TREATMENT DURABILITY



2. VULCANISED RUBBERS (SBR, NBR, etc...)



Adhesion value= 13.1 kN/m (M)

3. EVA copolymers (microporous)

EVA copolymers. They are the result of copolymerization process between polyethylene and vinyl acetate. High vinyl acetate content facilitates the compatibility with polyurethane adhesives.

Usual treatment:

–Microporous EVA: Application of polychloroprene primers on the surface and latter use of polyurethane adhesives or polychloroprene adhesives.

–Disadvantages:

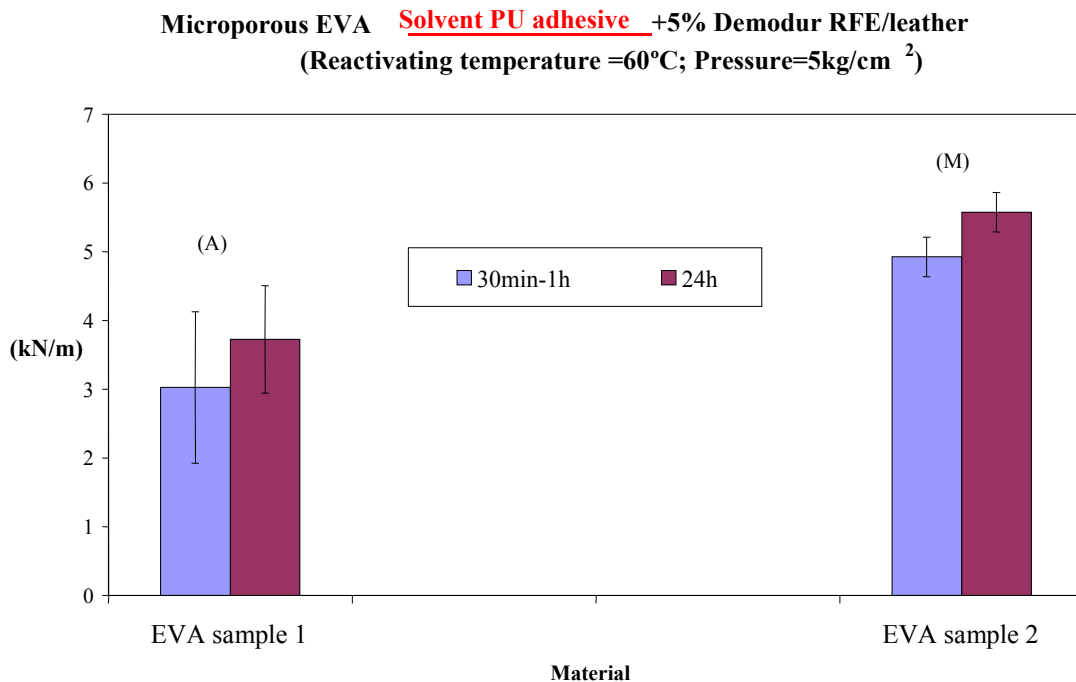
<Incompatibility with polyurethane adhesives

<Use of polychloroprene adhesives (contact glues), that present low temperature resistance and contain toluene and *n*-hexane in their formulation

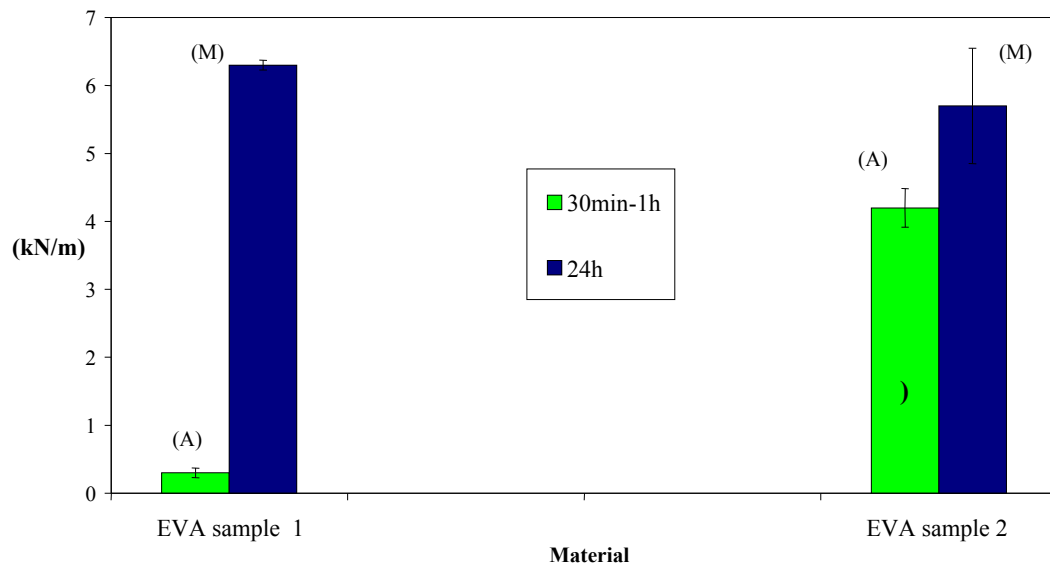
CT-100 treatment for microporous EVA: Good adhesion after roughing and direct CT-100 treatment with solvent or water-based polyurethane adhesives.

Treatment durability without adhesive: 1-2 weeks

Results obtained from commercial formulations tested in laboratory



Microporous EVA **WB PU adhesive +5% Demodur RFE/leather**
(Reactivating temperature =70°C; Pressure=5kg/cm



III. Recomendations for the CT-100 treatment

- For the correct use of the CT-100 surface treatment, useful for a wide variety of materials and formulations employed in the footwear industry, here are some recommendations:

- Whenever it's possible, the surface materials should be analysed to find release agents or other adhesive compounds, and at the same time to recommend the best surface treatment conditions for each material.

- To carry out the joints, the addition of isocyanate to the adhesive is recommended, even in case of materials where it's not necessary.

- For a total effectiveness and absolute security of the joints, it's recommended to carry out the adhesion process during the working day, specially when working with soles of SBR rubbers with low hardness and high content of waxes and oils. These compounds migrate to the rubber surface with time and can cause adhesive problems.

- Pay attention to all steps of the adhesion joints formation:

1. Adhesive reactivation: Use of infrared heater (*flash*) and surface temperatures near to 80°C or higher is recommended.

2. Pressure: the intimate contact between the materials to be bonded, as well as the pressure employed, are critical to obtain successful adhesive joints.

IV. Bonding security and joints normalization

CT-100 treatment system provides a big security of bonding, being a quality control of the adhesive joints carried out following the indicated recommendations.

In the laboratory of CELTECNIA S.L. we carry out as many tests as needed to assure the bonding quality in the production lines and to obtain complete customer satisfaction. T-peel strength measurements in universal testing machine and accelerated ageing in climatic chamber are performed for each model.

In the laboratory, the most effective CT-100 surface treatment for each material will be determined. The soles provided by the customer are treated and bonded. Later the adhesive strength is evaluated, being as important the final adhesion value, when the adhesive is completely cured (24-72h), as the initial adhesive strength value (1-2min), to guarantee the joint strength in the pressing process and to remove the shoe from the press, when the joints suffer considerable peel stresses. Additionally, ageing test in climatic chamber (humidity and temperature) is carried out to evaluate if both the treatment and the adhesive can resist adverse environmental conditions.

In all cases, the CT-100 surface treatment recommended to the customers, adapts to their bonding necessities, like treatment durability (time between the surface treatment and the adhesive joints formation in the shoes production line), which adhesive should be employed, the characteristics of the production, like reactivation temperature and kind of heater (infrared radiation or resistance), the pressure to be employed and kind of press, the characteristic of the upper materials (if leathers are roughed, if contain primers, their heat resistance (to avoid deformation, change of colour...), etc.

After working with the CT-100 system, all our customers are conscious that being careful in all steps of the bonding process is critical (treatment, application and kind of adhesive, reactivation, pressure...) and that the process optimization produces adhesion security.

The use of CT-100 system is very easy and in collaboration with CELTECNIA S.L staff, it guarantees an optimum bonding process. In a short time, the customer is able to carry out his own tests with new models, always obtaining excellent adhesive joints.

V. Usual terminology in the footwear industry

- **Contact adhesives**: Polychloroprene based adhesives, which due to the high content of resins present tack during sufficiently time and do not require reactivation, being very suitable for set up operations, which are not require high final strength.
- **Plastic adhesives**: Polyurethane adhesives, which are normally solved in ketones (mek or acetone) to be easily applied. To carry out the adhesive joints is necessary that the solvent evaporates, then the adhesive loses its tack and requires reactivation by furnaces (resistances) or by infrared lamps (flash heater) to recover it.
- **Desmodur**: Commercial name employed by Bayer, to refer to its range of isocyanates (hardeners). Isocyanates are compounds that are very reactive with polyurethane and polychloroprene adhesives, increasing the curing speed and the resistance to humidity and temperature.
- **Primer**: In footwear industry, primers are polyurethane and polychloroprene adhesive solutions, with lower solid content than the adhesives used to perform final bonding, which present higher adhesion strength.

Primers are adhesion promoters and increase the compatibility between the material surface and adhesives, paints, and other coatings. Some examples of primers are carboxylic acid, titanates, silanes...

VI. Environmental and workplace health

The commonly performed preparations of soles for adhesion, use malicious chemicals for human health and environment.

Not only halogen component, but also volatile organic compounds (VOC) are malicious.

VOC's, volatilise easily. Practically all VOC's are toxic by inhalation and by contact, transported by blood, and can cause damage to nervous system and liver. In fact, there is a known syndrome related with VOC's, called "footwear paralysis".

Given this risk, an entity related to footwear companies has emerged, which is going to take a sampling in some factories to control the amount of solvent used in this sector.

The application of chemicals that improve adhesion must be done under current regulations, in suitable conditions, following security laws, using equipment such as extraction hoods, safety masks, latex gloves, and other personal protection gear.

Besides the risks for worker's health and environment, there is also a problem about residues and containers.

In accordance with Valencian laws, these residues are dangerous, so they must be stored and labelled properly, and it is necessary to have an expert residues agent to handle them.

The use of clean technologies, as the one we introduce, reduces the use of VOC's in manufacturing process.

As it is known, an European guideline has limited the emission of VOC in production processes. If we put together CELTECNIA S.L technology for surfaces treatment, and CELTECNIA S.L water based adhesives, we can eliminate the use of organic solvents in adhesive process.

So, this technology, helps businessmen to accomplish current regulations about workplace health and environment.