

AIM OF THE PROJECT WORK

The aim of my project work is:

- To analyze the sole bonding of EVA sole.
- To find out the market value of PU and Neoprene adhesives and *EVA* sole.
- make a quality footwear.

The project work also has the following objectives:

- May cause little awareness the people related to footwear export.
- To give a rough idea about the PU and Neoprene adhesives for the sole bonding of EVA sole.
- Find out the weakness and potential of my project > It may be made an effort to find the problem related to the manufacturing of footwear and their remedies.

CHAPTER-1

1.1 INTRODUCTION:

Over the last 40 years there has been a major change in soling materials used in the Footwear trade. Leather has been the traditional soling material for Footwear. But in 1980 only about 5% of shoes have leather soles. Nowadays most soles are made of rubber or plastics which are classed as synthetic soling materials. So new types of soling needs new types of adhesion method or technique with different types of upper materials.

The scientific study of adhesion is quite new and its name, Zygology, is scarcely known. Zygology is the science of joining things which includes the study of adhesion and of welding, riveting and all forms of mechanical jointing. It includes the principle of -

1.2 Specific adhesion: It gives a chemical bond between the adhesive and the surfaces being joined. The adhesive, therefore, does not have to penetrate the material but is bonded to the material by chemical action.

1.3 Mechanical adhesion: It gives a physical bond which the adhesive 'keys' in to the fibers or structures of the material to be bonded.

Chapter-2

2.1. ADHESIVE

These are materials used for attaching by means of an adhesive. Shoe uppers, soles, toe puff etc. are a few examples for adherend or substrates.

HISTORICAL DEVELOPMENT OF ADHESIVES AND ADHESIVE BONDING:

The history of adhesive is closely related to the history of human kind. Although most of these materials have been subject to vast changes, others have been changed very little over time. As new materials are developed, a review of the history of uses can lead one to see where they might be applied to improve old applications, and sometimes to satisfy requirements of entirely new applications.

Modern Adhesive:

From the earliest days, the materials that we, later called cements, glues, gum, mucilage, resins, pastes, and finally adhesives were used interchangeably.

Historically, the first thermoplastic synthetic adhesive was the cellulose ester, cellulose nitrate, often called nitrocellulose, and it is still one of the most important.

There is little agreement in the literature about the dates when various adhesive were first development or used in a specific application. This is due to simultaneous developments in many parts of the world and the fact that references in the literature are almost exclusive from the more developed countries.

Synthetic rubber, a dimethylbutadiene, was developed as a substitute for natural rubber and saw limited use as an adhesive but today SBR adhesives are the most important adhesive in the USA. Neoprene rubber adhesive are available as both thermoplastic and cross-linkings\stems in both solvent and emulsion formulation. Neoprene rubber is the major base resin for contact adhesives.

Most of the thermoplastic resins were soluble in organic solvents and were used as solvents adhesives for different materials. PVC, a thermoplastic developed in 1927, is used today in solvent formulation to bond PVC article such as coated fabrics, films, foams and pipe.

PVC was used as a solvent-based adhesive in the 1930s, and later as a hot melt, but was not of commercial importance until its introduction in the 1940s as an emulsion adhesive. Today, in emulsion form as a white glue, it is the most widely thermoplastic adhesive worldwide. Today acrylic adhesive appear in many forms; as both pressure sensitive and non-pressure sensitive formulation in organic solvents and emulsion forms.

Polyurethane adhesives are polymers produced by addition reactions between polyisocyanates and hydroxyl-rich compounds (at least two hydroxyl groups per molecule) such as glycol, polyesters, polythene. Today, PU adhesives are available as solvent-based moisture adhesives, thermoplastic, hot melts, thermosetting systems and emulsions.

Today even in the most developed countries, natural adhesives dominate the market because they are less expensive than synthetic based materials, and they perform the intended function. Natural rubber is still the most widely used based materials in pressure sensitive adhesives. Natural rubber solvent solution adhesives are widely used throughout the \world as general purpose-adhesives.

Adhesion began to create interest in scientific circles only about 50 years ago. At the time adhesion became a scientific subject in its own right but still a subject in which empiricism and technology are slightly in advance of science, although the gap between theory and practice has been shortened considerably.

IMPORTANCE/USE OF ADHESIVES IN LEATHER GOODS MAKING:

Adhesives form an important part of leather product chemicals in general and shoe chemicals in particular. Adhesives used in leather goods are for two purposes-Temporary and Permanent joint. Most of the leather goods require temporary joint while assembling; and they are stitched later to be permanent for the end use. So water based latex and rubber solutions serve the best result for this purpose. Other kind of products is made only by using adhesives; so permanent joint is achieved with it. Solvent based polychloroprene and polyurethane serve the best result in this respect as they are permanent types.

Natural rubber makes strong adhesives which have proved their suitability time and again for shoe trade operations; but of the synthetic materials can give as strong an adhesion and are not as susceptible to be attacked by grease and oxidizing agents.

CLASSIFICATION OF ADHESIVE:

There are mainly two types of adhesive:

- a. Water based adhesive
- b. Solvent based adhesive

a. Water based adhesive are:

1. Natural rubber latex
2. Synthetics lattices
3. Vegetable paste

1. NATURAL RUBBER LATEX

Natural rubber is a product existing as a milky substance known as latex. It is obtained from “Heveabraziliensis”. Latex is a colloidal dispersion of rubber particle in water.

Basically, latex is tapped from the rubber tree. But usually compounded with resins to improve tack. Contains ammonia for stability.

PROPERTIES:

1. Non flammable
2. Good initial grab
3. Clean in use
4. Spray able
5. Low plasticizer resistance
6. Versatile bonding method
7. Poor heat resistance.

USES:

1. Fitting, Laminating, Folding
2. Toe puff attaching
3. Stiffener attaching
4. Insole binding
5. Socking
6. Heel covering

2. SYNTHETICS LATICES:

It is obtained from emulsion or dispersion of synthetic polymer such as polyvinyl acetate (PVA), acrylate, polychloroprene or polyurethane (PU) in water.

PROPERTIES:

1. Non flammable
2. Relatively poor wet “grab”
3. Superior plasticizer resistance.

USES:

1. Socking
2. Toe puff attaching
3. Stiffener attaching
4. Heel covering

3. VEGETABLE PASTE

It is made from starch that is a derivatives of starch.

PROPERTIES:

1. Non flammable
2. Low bond strength
3. Soften by water

USES:

- 1.Box leveling

b.Solvent based adhesive are:

1. Rubber solution
2. Polychloprene solution (Neoprene)
3. Polyurathane

1. RUBBER SOLUTION

It is prepared by milling latex together with the compounded rubber and dissolving the same in a solvent such as benzene or gasoline. A resin tackifier is also used.

PROPERTIES:

1. Generally flammable
2. Good tack but not high strength
3. Limited plasticizer resistance
4. Moderate heat resistance
5. Sensitive to oil and organic solvents

6. Petroleum solvent based solution unlikely to damage material

USES:

1. Upper to lining attachment
2. Sock lining to insole attachment
3. Temporary bonding for edge folding

2. POLYCHLOROPRENE SOLUTION (NEOPRENE)

Polychloroprene is a synthetic elastomer with many of the properties of natural rubber. These are prepared in number of grades depending on the crystallization rate.

PROPERTIES:

1. High bond strength
2. Good grab
3. Limited plasticizer resistance
4. Easy handling
5. Can use with brush or spray
6. Difficult to remove if materials are contaminated
7. Long tack life

USES:

1. Fitting, laminating
2. Insole laminating
3. Insole rib attaching
4. Rubber and leather sole laying
5. Lasting
6. Heel covering

Ingredients used in polychloroprene adhesive are:

- i. Resins
- ii. Antioxidants

- iii. Solvents
- iv. Fillers
- v. Accelerators
- vi. Cross linking agents

3. POLYURETHANE

Polyurethane is produced when a di-isocyanate having two isocyanate groups is reacted with a diol having two hydroxyl groups.

Ingredients used in the formation of PU are:

- 1. Polyols
- 2. Di-isocyanate
- 3. Curing agents

CLASSIFICATION OF POLYURETHANE:

- 1. Reactive adhesive
- 2. Hydroxyl solvents adhesives
- 3. Aqueous dispersion

PROPERTIES:

- 1. Flammable
- 2. Strong bond with most material
- 3. Superior plasticizer resistance
- 4. Grease and oil resistance
- 5. High green strength but at least 48 hours needed to reach full strength
- 6. Difficult to remove if materials are contaminated

USES:

- 1. Sock attaching
- 2. Sole attaching

2.1.1. POLYURETHANE (PU) SOLUTIONS;

Form Solution of PU polymer in ketone and other solvents.

Properties

- Flammable
- Superior plasticiser and grease resistance
- Limited cold tack life
- Strong bonds with most materials
- Difficult to remove if materials are contaminated

Operations in which PU solutions are used are listed, together with any associated problems are given below:

Operation	Application method	Problems	Cause/remedy
Hand lasting (e.g. with PVC uppered sandals)	The adhesive is usually hand brushed onto the upper and margin; after drying the bonds are made by heat activation of one or both coated surfaces,	Poor bonds caused by inadequate tack.	Increase heat activation of the adhesive coated surfaces.

Rand attachment to soles (PVC rands in particular)	The randing is roller coated with adhesive, generally just prior to attaching, and the sole also roller coated either overall or just around the margin. After drying, the rand is laid on the sole	Poor adhesion to sole or rand material. Poor coalescence between adhesive films.	Check that correct preparation of material has been carried out prior to cementing. Check machine Setting for Application of Adequate heat and pressure.
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2.2PRE-TREATMENT (Primers):

To obtain satisfactory bonding between two materials using an adhesive normally requires some form of surface preparation to improve the adhesive between the cement and the material surfaces.

This may involve

- (i) Physical treatment (e.g.-roughing)
- (ii) Chemical treatment
- (iii) A combination of both. Chemical primers may be classified as follows:

2.2.1(i) Cleaners (Solvent wipes):

These are solvents which remove greases, oils, plasticizer, mould release agents, oxidation (ageing) products and other contaminants which could reduce adhesion or weaken the adhesive. They will also make the surface more easily wetted by the adhesive.

2.2.2(ii) Fillers:

These types are used to prevent bond starvation caused by excessive absorption of adhesive into the porous surfaces like leather and fabrics. Examples are Bostic 123 and 194.

2.2.3(iii) Modifiers:

This type is mainly used on rubber and plastic materials. These tend to be less compatible with adhesive than fibrous surfaces. A polymer film is deposited from sole which acts as an intermediate layer, forming a strong bond to both material and adhesive. Each modifier is designed to be used with a particular adhesive, Examples- Bostic M927 & 170.

2.2.4(iv) Activators:

This type of primers activate a surface so that it can form strong chemical bonds to the adhesive. They are much more hazardous to use than other primers. In most cases their activity is destroyed by moisture, so containers should be kept sealed and adhesive applied to the primed surface within a specified time limit. Examples are SATRA formulation SDP102, Bostic 313.

2.3. THE ADHESIVE BOND:

2.3.1. Mechanisms of Adhesion:

There are two main mechanisms by which an adhesive (cement) sticks to a material. These are referred to as Mechanical Adhesion and Specific Adhesion.

2.3.1(a). Mechanical Adhesion:

This is the more common of the two, being effective to some extent in almost all examples of bonding. Many materials have visibly rough surfaces. smoothest surfaces contain microscopic pores.

When adhesive is applied in liquid form to the surface, some of it flows into these pores. After drying, the adhesive layer will be 'keyed' to the material surface rather like two pieces of a jig-saw puzzle are joined together.

The effectiveness of the bond will depend on the strength of the material, and on the size, depth and shape of the pores. Deep and under-cut pores will lead to stronger bonds than shallow indentations.

Good bonds can be formed to fibrous surface because adhesive can surround the fibres. In most bonds there is some degree of mechanical adhesion present. Examples are PU, polychloroprene or latex on leather, fabrics and rubber soling.

2.3.1.2b) Specific Adhesion:

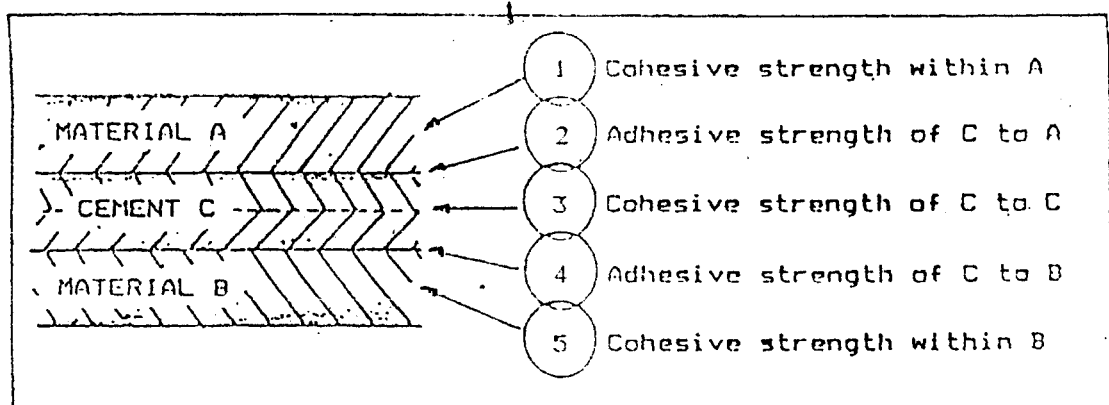
On a molecular scale, bonding occurs. when adhesive molecules diffuse into and become intertwined with the molecules in the material surface. For this to happen the attractive forces between adhesive molecules and material molecules must be at least as strong as the attraction of adhesive molecules for each other. i.e. the adhesive is more specific in what it will bond to.

The diffusion process is helped by the presence of solvents in the adhesive which swell or partially dissolve the material surface. Heat performs a similar function when using hot melt cements, and when causing one cement film to coalesce with another after reactivation.

In another type of specific adhesion the molecules in the cement become bound by strong chemical bonds to molecules in the material. For this to happen there must be specific chemical structures present in the two bonding surfaces. Frequently the material surface is made chemically reactive to the cement just before spreading by applying a

special primer. An example is the use of a halogenating agent on thermoplastic rubber before applying PU cement.

2.4 Links of Adhesion:



It is possible to identify 5 areas (links) within an adhesive bond which contribute to its strength. The bond will only be as strong as the weakest of these links. To ensure that each link is as strong as possible, the correct bonding procedures should be followed. The account below is particularly relevant to sole bonding, but is applicable to any type of bond.

Links 1 and 5

Weak layers within materials A and B must be removed by roughing or scouring, e.g. The grain layer from leather, the PU layer from PU coated fabrics (PUCF's) and, sometimes the surface layers from vulcanized rubber (VR) soling materials.

Links 2 and 4

Satisfactory adhesion of cement C to both A and B depends on a number of factors:

a) Correct surface preparation:

- i) Roughing / Scouring increases the number and depth of surface pores. This gives better mechanical adhesion to most

materials but care must be taken not to overdo it, and to remove all loosened material before applying the cement.

- ii) Solvent wiping removes surface contamination such as grease from leather, plasticizer from PVC, mould release agents from soling materials and soaps in VR. It also improves surface wetting by the cement.. With rubbers and plastics, suitable solvents can soften and swell surface layers to facilitate infusion of cement.
- iii) Chemical printing makes a surface more compatible with certain cements by chemically modifying it. e.g.. 'satreat' for chlorinates crepe, VR and Thermoplastic :Rubber (TR) to allow some specific adhesion to PU cement. Isocyanate primers improve specific adhesion to Nylon, Polyester and Ethylene Vinyl Acetate (EVA). A special primer for EVA deposits a polymer film. Dilute cement solutions are used as primers on very porous surfaces to provide a better foundation for the main cement layer.

b) Correct selection of adhesive:

The adhesive must be compatible with both surfaces to be bonded. (Although not an absolute rule, it is normal to choose the same adhesive for A and B.)

c) Correct viscosity and surface tension:

Surface tension should be low to give better wetting of surfaces. V is costly should not be too high or penetration into small surface pores may be prevented. Too low a viscosity generally means that two or more coats will have to be applied on porous materials. The viscosity of water and solvent-based cements is determined by solids content, and of a

hot melt cement by its temperature.

d) Correct amount and distribution:

There must be enough adhesive left on the surface after drying, and it should be uniformly spread over the whole bonding area. e.g.. not too thin at the toe in a sole bond.

e) Correct drying time:

For full strength to develop, it is important that all traces of solvents from cements and primers are removed from the bond. This happens more quickly if the bond is left open to dry for sufficient time. Drying times depend on the type of solvent, the porosity of the material, the temperature and the efficiency of air flow.

With hot melt cements 'drying time' means the time it takes to cool and solidify. Since this is usually rapid, the 'drying' time should not be too long.

Open times should not be too long or the cement may become contaminated by dust, ageing etc.

Link 3

As well as correct preparation of surfaces and correct selection and application of cement, it is equally important that the bond is closed properly.

a) Correct reactivation temperature:

A weak bond will result if there is poor cohesion between the two cement layers. To avoid problems it is best to soften on or both dry cement surfaces by heating in a re-activator to the correct temperature. (85-90° for PU and Polychloroprene cements). N.B. the

bond must be closed immediately after heating.

b) Correct bonding pressure:

The pressure applied to the bond should be adjusted according to the softness of materials being bonded, Softer materials will need less pressure than harder materials. e.g.. too much pressure may cause permanent deformation of cellular soling materials. Too little pressure and harder soles will not conform closely enough to the upper.

N.B. In a press, it is the oil pressure fed to the hydraulic cylinder which is controlled. The cylinder provides the bonding force. The pressure created in the bond depends on the size of this force and on the bonding area. e.g. larger soles require larger forces to create the same bonding pressure, therefore greater oil pressures will be used on men's shoes than on ladies. Oil pressures for sole attaching vary from 2-7 Bar.

c) Correct pressure distribution:

Where the bond is not flat, as in most sole bonds, it is important to support the underside of the bond in such a way that the pressure is evenly distributed. Sometimes toe spring causes lower pressure and so poorer bonding at the toe. Most modern sole attaching machines have a means of blocking up the sole to the correct profile. An embossed aluminium foil is available from SATRA, which is used to check the pressure distribution in sole bonding.

d) Correct dwell time:

When pressure is applied to a bond the materials do not react instantly. Time is required for them to conform to each other. Dwell times depend on the elasticity and plasticity of the materials, but are around 9-15 seconds for sole attaching.

2.5 ALL ABOUT ADHESIVES

This is a measure of the ease with which a liquid adhesive will flow. The higher the viscosity the less easily it flows . Viscosity generally decreases with rise in temperature unless the adhesive is of the heat-curing type, in which case the reverse is true. Viscosity can also be decreased by addition of solvent thinners, or increased by evaporation of solvent. Together with its surface tension, viscosity controls the spreading and penetrating ability of an adhesive.

TOTAL SOLIDS CONTENT

This is the percent by weight of solid matter in an adhesive. Solid matter comprises the base polymer together with any other material which may be added to increase tackiness or reduce chemical degradation. The higher the solids content the more thinly need the cement be spread to obtain a good bond, and the more viscous it will be.

SHELF LIFE:

This is the expected storage life in unopened containers . It is determined by the stability of the adhesive at the storage temperature to chemical and physical changes.

POT LIFE:

With 1-part cements it refers to the maximum usable life after opening the container. With solvent cements it is almost impossible to re-seal containers efficiently and solvent will be lost by evaporation more or less slowly depending on volatility. It can of course be replaced, but if this is not done the liquid becomes too thick and lumpy to reconstitute effectively. Rate of solvent loss when a container is in use depends on its dimensions. In general the pot life will be longer if the container is narrow and deep rather than wide and shallow.

There are applicators available designed to reduce evaporation to a minimum. Some adhesives are affected by exposure to atmospheric moisture. With 2-part cements, pot life refers to the maximum usable life after mixing the two components. The mixing initiates a chemical reaction which results in the adhesive eventually becoming solid. Rate of reaction depends on the chemical nature and amount of 'hardener' used, temperature, and total amount mixed. In general the greater the proportion of hardener and the higher the temperature the faster is the reaction and the shorter the pot life. The reaction produces heat. The greater the amount mixed the harder it is for the heat to escape and the higher the temperature rises. Consequently the faster the reaction proceeds and the shorter the pot life.

DRYING TIME

This is the time required for a spread cement film to lose sufficient water or solvent for a successful bond to be made. It applies mainly to water or solvent based cements using a two-way dry stick method. The times are normally given for natural drying (at room temperature) but can be reduced considerably by passing coated components through hot air tunnels. - The higher the temperature and the better the air circulation the faster the drying rate. Drying times are shorter for films on porous materials like leather and fabrics than on non-porous materials like PVC, VR, TR etc.. The thicker the film the longer the time Failure to allow sufficient drying time will result in bonds with poor green strength and likely to 'spring back'. With hot melt Cements, there is no drying time because there is no solvent. For liquid curing adhesives, drying time refers to the time taken for the film to develop sufficient tackiness (spotting tack) for efficient bonding using a minimum press time.

As a general rule the shorter the drying time the shorter is the pot life but the more cost-effective is the bonding process.

PRESSURE-SENSITIVE LIFE

This is the time after drying that a cement film retains enough tackiness for a bond to be made by applying pressure alone to the components. Dry tack of many adhesives can be increased by the addition of various resins.

The pressure-sensitive life of cement films is reduced by the presence of dust in the air. Many cements have- no pressure-sensitivity once dry.

TACK RETENTION TIME (REACTIVATION LIFE or TACK LIFE)

This refers to the maximum time after drying that a cement film can be successfully reactivated by heat for good bonding. For some time after the pressure-sensitive life of an open film has expired, tackiness can be recovered (or generated) by heating the surface of the film to the correct activation temperature. Tack life is reduced by dust and ageing, and can sometimes be extended wiping the film.

OPEN TIME

This term is 'used by some people to mean tack life. Here it refers to the actual time which elapses between applying the adhesive and making the bond in the shoe factory. It depends on the work organization. Maximum open time should not exceed the tack life of the cement.

SPOTTING TACK

This refers to bond strength developed when two cement films are lightly pressed together. It should be sufficient for the components to remain in place while they are transferred to the press; but not so high

that the components cannot easily be re-positioned if necessary before applying full pressure.

COALESCENCE

This refers to the joining of two cement films. If coalescence is not efficient (due to expiry of tack life or failure to heat activate properly) the cohesive strength of the bond will be poor.

GREEN STRENGTH

This is the strength of a bond immediately after leaving the press. Full strength rarely achieved at the time of bonding owing to the presence of traces of solvent which have a plasticising effect. It would be uneconomic to wait until all solvent absorbed by porous materials has evaporated before making the bond (and may cause the tack life to be exceeded). With 2-part (curing) cements the chemical reactions slow down as they approach completion, and only when they are complete will full bond strength be reached. Green strength should be at least 80% of full strength to allow the shoes to continue without delay through the factory. Even under these conditions, it may take from 2 to 7 days for the full strength to develop.

PRESS TIME

This is the minimum time for which the components must be under pressure in the bonding press.' It is determined by the rate of set-up.

BONDING PRESSURE

This is the recommended pressure to be applied to the particular combination of materials and adhesive in. the press to achieve the best results. It controlled by the coalescent properties of the cement and the

compressive properties of the materials e.g. Expanded soling should not be subjected to as high a pressure as harder solid soling because of the risk of permanent deformation. Up to a point, the higher the pressure the stronger the bond.

RATE OF SET-UP

This is the speed with which green strength develops in the press. It is influenced mainly by the chemical and physical properties of the adhesive system. For dry stick methods the set-up should be rapid to reduce "press time. With wet stick 'methods the set-up needs to be slow to allow components to be positioned correctly after making the bone (e.g.. stiffener attachment and socking) .

CO-HESIVE STRENGTH

This is the bond strength between one cement film and another.

ADHESIVE STRENGTH

This is the bond strength between an adhesive film and a material.

BOND STRENGTH:

This refers to the overall strength of a material / cement / material combination. It requires that cohesive strength, adhesive strength and the materials strength should be satisfactory. A bond is only as strong as its weakest link.

2.6 HOW ADHESIVE WORK

In simple terms, materials are held together by attractions ('magnetic forces') between the atoms and molecules from which they are built up. The same forces might reasonably be expected to cause materials brought into contact to stick together.

Unfortunately, just as a toy magnet will only attract a pin at close range, intermolecular forces only operate over very short distances (one millionth of a mm!), so the necessary close contact is never achieved even with highly-polished surfaces.

Adhesive must wet surfaces

An adhesive overcomes the problem by making intimate contact with the surface; it does so by being applied as a liquid which will flow and wet the material to be joined.

How a liquid can create adhesion is easily demonstrated—a little spilt drink between glass and drink mat may cause the mat to cling when the glass is raised. However, very little force is needed to make the mat drop off again.

This brings us to the second fundamental requirement of an adhesive—having wet the surface it must develop strength to give a useful bonded joint. Strength comes from the setting or curing process during which the adhesive changes from liquid to solid.

Wetting followed by setting :

Wetting followed by setting, is common to all adhesive types. In addition, an adhesive must bridge the gap between the adherends to be joined and have an affinity for them.

The attraction of the adhesive molecules for the molecules at the material surface must be at least as great as the attraction of the adhesive molecules for each other. This compatibility of adhesive and Surface depends on the adhesive type and may be inherent, or achieved by pre-treatment of the adherend surfaces.

Bond must De-durable

For satisfactory service performance the finished adhesive bond must have adequate durability. For the service life of the product it must resist cyclic mechanical stresses, as in the flexing of shoes and heat, moisture and other media in the service environment.

Application may be as a solvent-based (solvent-borne) or water based (waterborne) solution; an emulsion or latex, usually water-based; a liquid chemical or a molten solid (hot melt).

2.7Several methods of setting and bond formation

Methods of setting or curing and bond formation include:

- Solvent/water loss after wet stick (wallpaper paste).
- Solvent/water loss followed by cold bonding (contact adhesive).
- Solvent/water loss followed by heat reactivation (most sole attaching adhesives).
- Chemical curing (epoxide, cyano-acrylate 'superglue'). Cooling of melt (hot melt).

Sole bonds require adequate 'green' strength

Shoe sole bonds are usually under stress immediately after bonding and long clamping times would be inconvenient in production.

Therefore heat is commonly used to reactivate one or both of the essentially dry adhesive layers before combining them to produce a bond which, after a short pressing time, will have satisfactory 'green' strength and resistance to any tendency of the sole springing away. The adhesives for this process require the ability to coalesce, so that the two films brought into contact after reactivation will form one by diffusion of the molecules across the interface between them.

2.8 DEVELOPMENT OF SOLE BONDING ADHESIVES

The development and use of solvent-based adhesives for sole attaching is linked with developments in adhesive polymers and footwear materials.

Polychloroprene adhesives capable of heat reactivation Adhesives based on Nitrile or poly-chloroprene rubbers were in use by the late 1940s with Polychloroprenes favoured because of their excellent coalescing properties.

The period 1950-65 saw the main growth of stuck-on sole attachment, as polychloroprene adhesives proved capable of heat reactivation days or even weeks after application, before bonding with short press times. This gives the stuck-on process an attractive degree of flexibility.

Polyurethanes introduced for bonding PVC

During the mid-1960s the footwear industry was taking a close interest in plasticized PVC soles and upper materials. Polychloroprene adhesives did not have good affinity for PVC and were susceptible to softening by the plasticizer. However, polyurethane adhesives became available with excellent adhesion to PVC and inherent resistance to grease and plasticizers and offered an alternative system. Halogenation primers increase versatility of polyurethane adhesive. A major impetus to the increasing use of polyurethanes arrived with the development by SATRA of the surface chlorination or 'halogenations' process for thermoplastic and vulcanised rubbers. This enabled them to be stuck standard polyurethane adhesive. Halogenation primers such as Satreat, suitable for use in the factory, and primers for other solings, such as EVA and Nylon, are now in use world-wide in conjunction with polyurethane adhesive. Shoe manufacturers were attracted by the possibility of a common adhesive type on a wide range of materials, subject to the correct surface pre-treatment. By the end of the 1970s, polyurethanes had ousted polychloroprenes as the predominant sole attaching adhesive in the developed world although polychloroprenes have continued in use where their good working properties are valued.

During the late 1970s special adhesives-both acrylic modified polyurethanes and polychloroprenes-were developed for bonding thermoplastic rubber. The modified polyurethanes are now often used with halogenation for added security, but the modified polychloroprenes see widespread use in Asia for sports and casual footwear.

Polyurethane adhesives

These are formulated from linear thermoplastic polyester polyurethane polymers dissolved in solvents, such as Methyl Ethyl Ketone (MEK), acetone and ethyl acetate to give a solids content of around 20% by mass, Chlorinated rubber and resins may be added to improve heat resistance or tack. Adhesives may be

One part : having no free iso-cyanate present.

Pre-reacted or premixed: Containing an iso-cyanate which reacts very slowly prior to application, allowing a usable shelf life of a few months.

Two part: In which a small proportion of an iso-cyanate curing agent is mixed in before use. These have a pot life of just a few hours and require a short open time. Free iso-cyanate, when present, is available to react; with and crosslink the applied adhesive film. It gives good heat resistance and may improve adhesion.

2.9 Polychloroprene adhesives

These are formulated from polychloroprene rubbers (such as 'Neoprene' and 'Baypren')- The rubbery polymers are dissolved in solvents such as toluene, petroleum and MEK to give a solids content of around 25%.

Essential additives are acid acceptors, such as *zinc* or magnesium oxide and resins to impart tack; the metal oxide and tackifying resin are usually reacted together before addition. Polychloroprene adhesives can be used in two-part form, with added isocyanate improving heat and grease resistance.

It is now possible to synthesise or disperse polymers to form a latex or emulsion, defined as 'a stable colloidal dispersion of polymer particles in an aqueous medium.' Particles, each comprising thousands of individual molecules but still very small (about one ten thousandth of a mm in diameter), are kept, in suspension by the action of stabilisers.

Because the polymer particles reflect light, the dispersion usually appears milk white. After application as a coating, dispersions dry by losing water, the polymer particles being forced closer together until they coalesce into a film. Chemicals, or traces of solvent, are often included in the formulation to act as coalescing aids.

Water-based adhesives have the advantage that they require a similar bonding process to solvent-based adhesives, so can be handled by familiar procedures. This has led to the steady growth in their use.

Polyurethane adhesives Dispersions of polyurethanes suitable for formulating adhesives have been available for more than 20 years.

Because a dispersion has molecules agglomerated as particles in the water, rather than individual molecules in solvent, viscosity of a water-based adhesive is inherently low, although it can be increased by thickeners. On the other hand, the solids content can be higher than with solvent-based adhesives-at about 40%.

A recent development is the production of iso-cyanate curing agents compatible with water-based polyurethane adhesives, enabling two-part systems to be offered. These are hard to conceive, as it is well known that iso-cyanates react readily with water. Again, chemistry has come into play, developing iso cyanates that 'like' the PU polymer more than water and react preferentially with it.

Polychloroprene adhesive : Polychloroprene dispersions are also well established, enabling adhesives for many purposes to be formulated. Like their solvent-based counterparts these usually require the incorporation of a compatible tackifying resin. They are used in shoe manufacture for temporary sole attachment in welted footwear and other ancillary operations.

Because aqueous synthetic polymer dispersions exist in an 'unnatural' state they are sensitive to various influences which can cause instability and irreversible coagulation of the polymer as rubbery lumps. This means that water-based adhesives should always be stored as recommended by the supplier, usually above 5°C (five degrees) to avoid freezing.

Additions of chemicals, including water, should never be made unless these are specifically permitted. Critical parts of application machinery must be of nonferrous materials and flow paths free of severe constrictions.

The main limitation of conventional hot melt adhesives (as used for lasting) is the relatively high viscosity, leading to poor wetting and penetration of leather and other fibrous materials. It is not feasible to use conventional polyurethane adhesive polymers in hot melt form.

Recent developments in reactive polyurethane hot melts have overcome the problem by applying a partially cured polymer as a low viscosity melt. The adhesive then further cures by moisture (or heat), before either direct bonding or heat reactivation. Final cure takes place after bonding.

Attention has had to be given to producing the optimum balance of wetting, tack, green strength and final bond strength.

Hot melts have the advantage of 100% solids content, making adequate adhesive coatings easy to achieve. However, they require special application equipment and this is perhaps the main reason why commercial usage to date has been limited.

2.10.SURFACE PRE-TREATMENT

Effective surface pre-treatment, is essential for good bonding. Pretreatments may be either mechanical, such as roughing or scouring, or chemical, such as solvent wiping and priming.

Both types may remove surface contaminants, remove or consolidate weak surface layers, or enable the material surface to be more easily wetted by the adhesive. In addition, chemical treatments may chemically modify the surface to give it greater affinity for the adhesive.

The main recent development in roughing of uppers is the introduction of computer-controlled automatic machines which are programmed to follow the lasted margin of each shoe style.

With the pressures to reduce solvent usage, cleaners based on detergent solutions or citrus oils have been introduced and water-based primers are under development.

2.11.A. ADHESIVE APPLICATION AND DRYING

Adhesive is applied by hand brush, pressure-fed brush, roller or extruder machines. Modifications to suit water-based adhesives are available; for example the substitution of foam rubber rollers for gelatine rollers, and use of stainless steel or plastics for parts in contact with the adhesive.

Use of computer-controlled application machinery is growing and applicator heads for water-based or hot melt adhesives have been developed.

Water-based adhesives are more difficult to dry than solvent-based adhesives, leading to developments in drying equipment with increased air movement and/or higher temperatures.

2.12.THE BONDING PROCESS

In much of the world, heat reactivation, before immediately spotting and pressing, continues to be the favoured method of sole bonding. Some modern equipment combines drying and reactivation with the warm dry components emerging from the dryer being heated immediately to the reactivation temperature. This facilitates two-way reactivation of both soles and uppers which is favoured with many water based adhesives.

There is also a move back to using longer wavelength infra-red energy for reactivation; the advantage being low sensitivity to surface colour, rather than the 'flash' reactivation which has been almost universal for many years.

In Asia the adhesive on soles and uppers is usually dried in successive warm air cabinets, followed by a reactivation stage giving a temperature sufficient for coalescence. The relative high amount of heat absorbed by the materials allows for a relatively long delay between heating and pressing.

Indeed, the soles of sports and casual footwear, after spotting, are often pressed in successive operations dealing with sidewalk, toe/seat and sole bottom, using simple presses in each case.

In conventional shoemaking the requirement to press the whole of the sole evenly in one operation has led to flat bed presses with self levelling pad boxes and diaphragm presses which envelope the whole sole.

2.13.FUTURE PROSPECTS

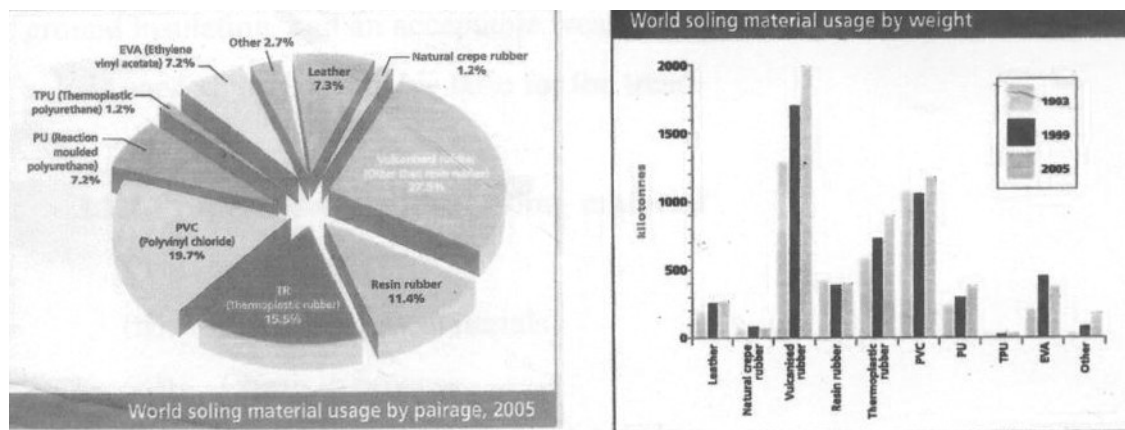
Most soles are attached to uppers by adhesive bonding, and it is inconceivable that this will not continue. The evolution of sole attaching adhesives to date has, fallen into three phases: introduction of solvent-based adhesives; adapting adhesives and pre-treatments to suit a wider range of materials; and development of solvent-free systems to reduce solvent usage.

The next phase is likely to see developments in reactive liquid systems with the aim of rapid, simplified bonding. Adhesive costs may be relatively high, but offset by savings in processing.

CHAPTER-3

SOLING

3.1.Sole: The sole is a critical component of any item of footwear. It protects the foot from the ground, and contributes substantially to the structural integrity of the shoe. The user must ensure that footwear chosen protects against the risks involved in the work place, that the styles and materials are compatible with the working conditions in terms of both withstanding the effects and protecting the wearer against them.



The performance of footwear depends on the overall design and construction. i.e.. the upper, lining, insole, midsole and outsole all contribute. The sole of a boot or shoe is important because it is in direct contact with the ground. It should help to:

- Provide the wearer with a stable base.
- Reduce risk of injury through shock when running, jumping etc.
- Provide traction and reduce risk of injury through slipping.
- Give insulation from sharp projections on the ground,
- Give heat insulation.
- Provide an acceptable wear life under specified conditions.

The relative importance of these factors depends on the purpose of

the footwear, e.g.. Indoor slippers, town shoes, industrial safety footwear, army boots and sports shoes all have very different requirements. Even the design of a sports shoe sole will depend on the type of sport. Rock climbing, fell walking, skiing, jogging, squash, football etc.. all involve different types of movement on different types of ground surface.

In spite of the diversity of applications, it is possible to give some general design guidelines. The following applies mainly to moulded sole units, but is also applicable to direct moulded soles and to sheet soling.

3.1.1.Soling Thickness:

The thickness of a sole must be sufficient to provide an acceptable level of ground insulation, and an acceptable wear life. A minimum of 2mm in any type of sole is needed to give a stable base for the tread.

3.1.2.Properties of an ideal soling material: Processing needs:

- Low cost raw materials.
- Cheap to process.
- Easy to mould with good definition.
- Form strong bonds with conventional adhesives
- Can be recycled

Wearing needs:

- Low density (light weight for comfort)
- High elasticity (Soles must not spread especially in hot conditions)
- High resilience (for energy return)
- High flexibility (for comfort in walking)
- Good flex crack resistance, especially in cold condition

- Good wet and dry slip resistance (for safety)
- Good abrasion (wear) resistance.
- Good water resistance (for comfort)
- Good rest resistance.
- Good cushioning ability (for comfort)
- Good shock absorption (to protect wearer from injury)
- Good ageing resistance.
- Good appearance.

3.2.TYPES OF SOLING MATERIALS

There are different types of soling materials. They are:

1. Leather
2. Leather board
3. Resin rubber
4. Vulcanized rubber-solid -cellular
5. Crepe rubber
6. Thermoplastic Rubber (TR)-1.Solid , 2.Cellular
7. PVC (Solid)
8. PVC (Cellular)
9. PVC (Blends)
- 10.PU reaction moulded-1 Cellular, 2. Solid
- 11.Thermoplastic PU-1.Solid, 2.Cellular
- 12.EVA (Cross-linked)
- 13.EVA (Thermoplastic)
- 14.Nylon (PA)
- 15.Polyester, solid, units
- 16.Polycarbonate.
- 17.Hytrel (EEC thermoplastic Elastomer)

3.3.IDENTIFICATION OF SOLING MATERIALS

Leather (vegetable tanned)

- Unmistakable smell.
- Soles often labeled leather with the hide mark.
- A fairly hard material.
- May be lightly embossed but no tread, usually has smooth, slick lightly glossed surface finish.
- Magnification reveals tiny pin-prick like hair shaft openings. A cut edge will reveal the fiber structure of leather.
- Generally tan colored but sometimes has a colored finish.
- Mostly found on formal and dress footwear. Some limited use in specialist industrial footwear.
- Light grey leather, often with a sueded surface, is probably chrome tanned and used in dance and 10 pin bowling shoes.

Vulcanized rubber (VR) (solid)

- Rubbery smell familiar to most people.
- Rubbery feel (grippy).
- Very good appearance with excellent definition of edges and fine detail.
- Mat surface finish or slight sheen.
- All colors possible including natural translucent.
- Very soft versions sometimes labeled 'Latex'.
- Often found as an outsole combined with a softer PU or EVA midsole. Soles which are VR only are relatively heavy,
- On industrial footwear may be marked 'heat resistant'.

TR (thermoplastic 'rubber')

- Superficially similar to vulcanized rubber
- Carries a distinctive synthetic smell which is quite different from VR.
- Very rubbery feel (grippy).

- Quite soft as judged by easy indentation, but surprisingly stiff.
- Sheened surface finish.
- Available in all colours.
- A less even quality of appearance than VR with some hairline moulding
- `Flaws' apparent in some locations on the surface.
- Not found with midsoles in other materials but sometimes two colour mouldings can mimic an outsole / midsole assembly.

PU (polyurethane) (reaction-moulded)

- Polyester type - no particular smell.
- Poly ether type - distinctive quite strong non rubbery smell
- Not a heavy material - lighter than solid rubber or PVC.
- May feel rubbery but often quite slick with a sheen to the surface.
- Has an expanded or microcellular structure, but this may not be evident as moulding produces a thin solid skin and usually there are no cut edges.
- Soles may be moulded with or without a tread pattern.
- A key feature is very small voids (caused by trapped air bubbles in mould) along the edges and at the corners of moulded detail such as tread cleats and lettering
- All colours possible.
- Often used in thicker soled footwear where it may be moulded to resemble cork or wood,
- Sometimes includes a softer, lighter PU midsole layer for extra cushioning and is then known as a dual density sole.

Natural Crepe rubber

- A translucent pale or honey coloured sheet material with a raw appearance. Wrinkled, textured or corrugated surface but no moulded sole profile or tread cleats.
- Quite soft and very rubbery with a distinctive slightly sweet smell unlike vulcanized or thermoplastic rubber.
- Cut edges show a layered effect at about 1 mm intervals.
- Clean fresh crepe will adhere to itself under pressure.
- Sometimes found in black or dark brown and sometimes pale crepe may have blacked or browned edges.
- Mostly used on comfort casuals.

Resin rubber

- A firm material, superficially leather-like, generally found as a thin sole on women's court shoes and fashion boots.
- No tread but winter boots may have a serrated forepart wear area.
- Usually has a glossy low friction (slick) surface finish but worn areas feel rubbery.
- Colour mainly black or tan to simulate leather, not translucent. Has good visual quality.

PVC ('vinyl')

- 'Plastic' vinyl smell familiar to most people.
- A relatively heavy material in solid form.
- Soft grades can feel rubbery, harder grades not.
- Fairly glossy, shiny surface.
- Tends to wear very smooth.
- Not found with midsoles in other materials but sometimes combined with a leather forepart in dress shoes.
- All-moulded boots such as Wellingtons are very often PVC.
- Cellular versions have reduced weight but same smell. They may have a solid skin with an irregular cell structure, or a uniform cell structure with a finely speckled mall surface.

EVA:

- Characteristic non-rubbery smell when new but this fades.
- An extremely lightweight material,
- Usually soft enough to be impressionable with a finger.
- May have a slick (moulded) surface- with a sheen or else a matt velvety surface which is a split through the microcellular structure. May have cut or moulded edge.
- Tread pattern often shallow, with better definition than PU (no small voids).
- Available in all colours, but not translucent.
- Generally good appearance, % _
- Often found as a midsole (shock absorbing) layer in sports shots,
- (Micro VR generally similar but smells rubbery and not quite so lightweight).

TPU (thermoplastic polyurethane)

1. Difficult to distinguish from PVC, but has no particular smell and the characteristic PVC smell will be absent.
2. Solid material feels smooth and not rubbery, microcellular materials are more rubber-like.
3. Mouldings have good definition, often with a matt finish.

3.4.A Fresh Look At Solings

Soling materials are available in a range of densities, weights, and chemical and physical properties. They may be cut from sheet, fabricated, or available in complex mouldings containing several colours and types of material.

The choice of soling for a particular shoe will depend on its overall design, colour, performance required and price.

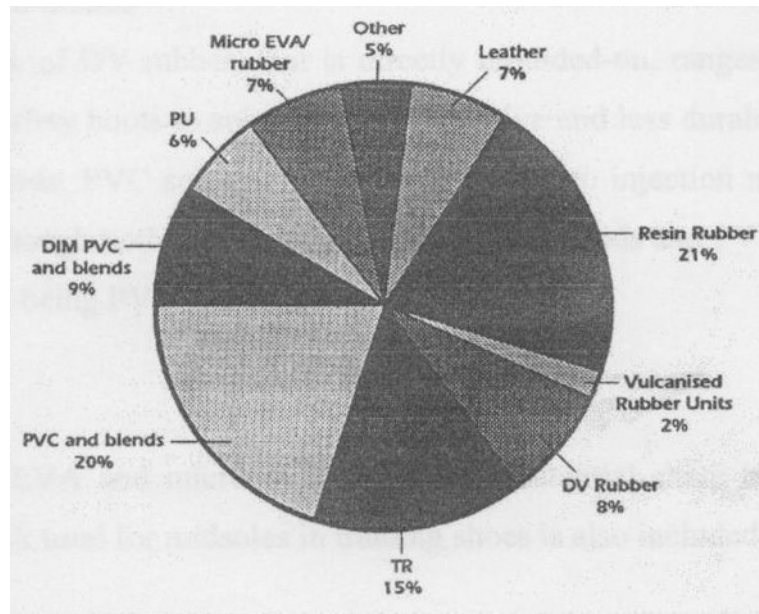


Figure 1. Soling types used worldwide

Certain styles of footwear have traditionally used particular types of soling, and perhaps footwear manufacturers and bottom material

suppliers could benefit from taking a fresh look at these established uses - looking at newer areas for traditional materials and vice versa.

Soling material usage

Figure 1 shows an estimated breakdown of solings used worldwide in 1991 in a total footwear production of some 10 billion pairs. Statistics like these are by their very nature quite broad and a few lines of qualification might be helpful.

Leather, the traditional soling, has been steadily replaced by newer materials which cost less and last longer. For example, the proportion of UK leather-uppered footwear with non-leather soles grew to about 90 per cent in 1990. Nevertheless, leather is still sought after for its aesthetic appeal and this is likely to continue for high class footwear. Specialty leather solings also meet the needs of some wear environments.

DIM PVC and Blends

The use of DV rubber, that is directly moulded-on, ranges from soles for high quality safety boots to soles for less expensive and less durable canvas shoes for summer wear. PVC soles are roughly divided into injection moulded-on and unit types, although both include straight PVC compounds and PVC blends - the most common being PVC/Nitrile rubber.

Leather

Micro EVA and micro rubber form a substantial share but it should be noted that EVA used for midsoles in training shoes is also included in 1.

Figure 1.

The PU category is mainly micro-cellular polyurethane, although some thermoplastic PU is included. All the major suppliers of polyurethane soling compounds - Bayer, Dow, Elastogran and ICI - have made strenuous efforts to replace CFCs (Chloro Fluoro Carbons) as the blowing agent, without affecting the performance of the soling.

The main difference is claimed to be in the shrinkage characteristics. With CFC blown systems, there is about 1.5 per cent shrinkage compared with 0.5 per cent for the water blown systems, which do not have a surface ski: For direct moulded footwear, this should not present problems but fitting tolerances will be affected in unit sole production. It is important to check the fit of sole units, produced in the same moulds, before switching to a CFC-free system. Where this presents problems, some suppliers have soft CFC systems available- with a much reduced ozone depletion potential- that have similar shrinkage characteristics to the standard CFC blown compounds.

3.5.Solings selection:

Solings are supplied in several forms, depending on the type of footwear being manufactured. They may also vary according to the manufacturing process, such as rubber vulcanisation, and the nature of the soling material, for example its thermoplasticity. The common forms are:

1. Sheet
2. Caster shapes
3. Built units
4. Moulded units
5. Moulded-on

One question which is nearly always asked in modern footwear manufacturing is how heavy the shoe will be. The trend is towards lightness-for comfort and performance- and so the term 'lightweight material' is frequently heard. Of course, this can mean low density, but it can also mean light in wear because of low soling substance.

It is probably better for the shoe manufacturer to be aware of the densities of the various soling materials on offer and then the weight of the sole will be thickness-dependent. Figure 2 explains graphically the range of densities available for most of the common soling materials.

Rubber-faced composite soles

A growth area is infills for dual density PU or rubber-faced composite soles, and infill density as low as 0.25g/cm^3 has been suggested for use with a mudguarded facer. Clear, translucent solid PU facers are of interest and can be produced by careful elimination of blowing agents such as water and compression of the reaction mixture in the mould .

In the Gusbi 'Newflex' process, a solid moulding with excellent surface definition, free from bubbles, is produced by applying high pressure after mould filling.

Lightweight Solings

A recent development in microcellular rubber solings is the production of oil resistance by incorporating nitrile rubber.

A major machinery development with microcellular EVA is the heat embossing of sheet material to produce patterned units .

Machines are available that produce units from sheet microcellular EVA by first softening with heat, then by forming between male and female moulds and finally cooling by refrigeration. BDF's approach is to soften the sheet, press and multi-cut.

Leather was a major constituent of a shoe i.e.. upper, lining..

soling etc.. were all made up of leather. Footwear industry started looking to other substitute material due to-

- Shortage of skin and hides and its consequent high price.
- Substitute materials offered better properties in manufacture and wear which leather could not offer, e.g.. synthetics are relatively uniform in thickness, surface and physical properties and are available in continuous roll form. '
- Substitute materials are cheaper to produce.

3.6.Substitute Soling Materials

A. Natural Rubber: Natural rubber was one of the first materials to be used in shoe soling application. Vulcanisation of the Rubber was discovered by Goodyear in 1839-40, followed and developed by Dunlop.

Vulcanised rubber is still used in casual & canvas shoes. Recently TPNR Thermoplastic natural rubber was developed in Malaysia to avoid vulcanisation process associated with Natural Rubber. TPNR is manufactured by blending of dynamically cross linked NR with PP. But commercially it did not succeed as it could not produce softer soling material below hardness of 70 shore, and also escalating natural rubber prices made it unattractive.

B. Synthetic Rubber: It was developed after researching on different synthetic materials and oils in 1920. By the end of World-II in 1945 SBR rubber was finally taken-up as a substitute for natural rubber.

In 1920 Bata started canvas upper with rubber soles in its FACTORY AT ZLIN (Czechoslovakia). Bata made canvas upper with moulded sole shoes in CENEL PRESS in 1935-45. Bata also developed rubber in

action moulding in 1955.

Microcellular rubber soles were developed in 1950 which was later called HAWAI in 1958. Bata developed BEIKUTE sole sheets from rubber which looked like leather sole sheet.

C. Thermoplastics

1) PVC- Polyvinyl chloride is a wonderful material which can be compounded to produce soles in various harnesses and can be compact or microcellular. But its higher weight makes it least preferred choice in high value high performance shoes. With the advent of SUPER - EXPANDED PVC now it is possible to reach a specific weight of 0.5, but this presents a poor resistance to abrasion and hence it is used only for seasonal articles such as beach sandals and slippers. The soles are produced on air blown machines using a foamed PVC compound.

2) TPR- Thermoplastic rubber is manufactured from oil bound Styrene-butadiene-Styrene block copolymer. Similar to PVC this material can also be SUPER-EXPANDED to produce light weight soles. This material can also reach a specific weight of 0.5 but has a fairly good resistance to abrasion and other characteristics appreciated by the sole market. Moreover, it lends itself very well to the two-material using a semi-compact TR for the outsole and a super-expanded TR as midsole.

3) EVA- Traditional System of Sheet Vulcanization.

Rubber v Polymers for Soling

There is a big market out there for soling materials. Global footwear production last year was around 11.5 billion pairs and is

estimated that it will be 12.7 billion pairs by the year 2005. Looked at another way, the soling market consumed some five million tonnes of materials through the late 1990s but is expected to expand to over six million tonnes by 2004, an increase of nearly 30 per cent in the ten years 1994-2004.

Leather was the first shoemaking material of note because it combined flexibility and moisture absorption with a degree of durability and water resistance. It could also be stitched and repaired and coloured.

Down the ages leather has main-tained its hold on the shoe upper market but in the last fifty years or so it has relinquished its grip in solings, today being confined to niche sectors and the highest quality footwear where price and durability are not prime considerations. Interestingly, with the exception of resin rubber, there appears to have been no attempt to simulate a leather soling material. Rather, new soling materials have stood on their own merits, being accepted for the aesthetic, performance and processing benefits they themselves offer.

The first real challenge to leather came with the availability of natural rubber in the 1930s. This offered good flexibility and greater durability than leather but was itself soon usurped by vulcanised rubber, introduced around 1940, which additionally offered considerable advantages in shoemaking.

Vulcanised rubber is still top

Its use provided, in fact, a genuine revolution in shoemaking. At a stroke, all the multiple sole attaching and finishing operations relating to leather soles, for example, were reduced to just one operation. Shoes made on the vulcanised process became the

favoured method of production for men's work boots and shoes, uniform shoes and military footwear, safety footwear and boys' and girls' school shoes.

The productivity gains using vulcanisation to attach the sole were very significant. The boots and shoes were also superior in comfort and durability to the heavy, riveted, screwed and stitched work boots of those days. Additionally, non-slip and resistance to chemical attack are two other valuable features.

Interestingly, development in the vulcanisation process is ongoing as seen in the vulcanising adhesive introduced last November by Caswell. Their new product is very stable and opens up new exporting possibilities because it will not quickly degrade during transportation or storage, even under adverse conditions.

The popularity and suitability of the vulcanising process to produce hardwearing footwear for service, military and safety footwear continues to this day. Indeed, vulcanised rubber is still the most used soling material with an estimated 27.5 per cent global market share by pairage.

This spectacular success has been achieved and maintained in spite of a somewhat longwinded and inflexible process which is still fundamentally unchanged from when it was first developed. But, equally significant, the vulcanising process, where the sole is attached and finished in one operation, opened up the route for later technologies, such as injection moulding, which are far more versatile.

PVC was the first injection mould-able soling material on the market, making its appearance in the 1960s. It is a low cost, easy-to-process, hard wearing material but in solid form it is somewhat heavy and its slip resistance tends to be low, particularly in harder grades. It

also suffers from a utility image and its traditional shiny appearance somewhat restricted its range of design possibilities. Nevertheless, PVC is used in over 25 per cent of all shoe soles and it remains the second most popular soling material after vulcanised rubber, commanding virtually 20 per cent of the global market.

Whether this will remain the situation in the longer term remains to be seen, from a recent presentation, SATRA said that PVC was chlorine-bearing and so perceived as being non-green, especially during production and disposal. It needed the addition of plasticisers to make it soft and flexible for soling applications-and these were usually of the phthalate type which are now thought to present health risks. Possibilities to overcome these problems include using alternative plasticisers, PVC blends or new polymers developed from biotechnology. All approaches were feasible but PVC would lose its cost advantage.

Range of soling materials doubles The 1970s saw a doubling of the soling materials available to the shoe manufacturer with the introduction of polyurethane (PU), thermoplastic rubber (TR) and thermoplastic polyurethane (TPU). Early PU soles experienced severe and widespread flex cracking which might, have led to the material being rejected by the shoe industry. But once it was realised that processing conditions were critical and the shoe manufacturer did not enjoy the latitude available in other soling systems, PU soon gained acceptance as a quality soling material with good performance characteristics and extensive design possibilities.

The 1980s saw the introduction of EVA which initially made its impact as a foam wedge and soon became a preferred midsole material because it was a lightweight material offering equivalent cushioning to heavier materials. Earlier processing methods were somewhat complicated but it can now be injection moulded.

The newest soling material is POE-polyole Of elastomer-a thermoplastic material which can be processed on conventional injection moulding equipment and is expected to take market, share from EVA, PVC and possibly PU.

Steve Lee, in a paper Footwear Market Overview, says the real growth in soling materials has been in thermoplastic materials such as PVC, TPU, TR, EVA and POE which can be moulded on conventional injection machinery. Their, other major advantage is the fact that any scrap material can be recycled which is not the case with thermoset materials such as vulcanised rubbers and polyurethane,

Mr. Lee also makes the point that the actual choice of soling materials available is, in fact, much, greater since these primary materials can also be compounded together. For instance, TRs normally contain EVA, and TPU and PVC are commonly blended together. Also it is becoming very common for several materials to be used to build up a complete sole. Examples. are VR/PU, VR/EVA, TPU/PU, TR/TR where the combinations refer to the outsole/midsole. In all cases, the midsole is a lower density than the outsole. One interesting combination, made possible by technical developments in the 1990s, is rubberpolyurethane direct, soling produced in one operation on an injection moulding carousel. First, rubber is injected into an open mould and is compressed. A lightweight PU midsole is then injected conventionally

The most, recent trend is towards blowing thermoplastic materials so that TK/TR, TPU/TPU, PVC/PVC sole combinations can be produced using; like materials with the midsole being low density.

VR and PVC will continue on top Looking to the future, SATRA anticipates that the overall usage of leather, natural crepe and resin

rubber are all likely to decline slightly in percentage terms though not necessarily in tonnage terms. In contrast, vulcanised rubber, PU, TPU and TK should while PVC will stay the same.

3.7. ETHYLENE VINYL ACETATE (EVA)

This material, produced by the copolymerisation of ethylene and vinyl acetate, is used for solings in both thermoplastic and cross-linked forms. The properties of polyethylene are well known, and the vinyl acetate part of the copolymer produces a material that is softer and more rubbery than polyethylene (polythene) .

Ethylene vinyl acetate is a tough flexible, lightweight (density 0.93-0.96 Mg/m³) essentially thermoplastic material that can be moulded to shape using the same techniques and machinery as are used for PVC. It can, however, also be cross-linked, compounded, processed, and moulded like vulcanised rubber. Because it is more expensive than natural and synthetic rubbers, the cured form of EVA is usually offered only as a microcellular material, where its initial low density, ease of processing and moulding, together with appearance and handling benefits can offset the initial high cost of the raw EVA polymer.

As the thermoplastic version is offered in cellular as well as solid form, considerable confusion has sometimes arisen when dealing with these two materials.

For shoe manufacture, the cross-linked microcellular version is available only in sheet or prefabricated sole-unit form, as is microcellular rubber. The thermoplastic version is available in granules or moulded-unit form, and so the confusion need not arise.

A common density of EVA is 0.3 Mg/m³. At this density, the specific durability can be as good as microcellular rubber with a density of about 0.6. This does not necessarily mean that the two solings

are direct competitors. Microcellular rubber is still preferred where durability is more ore important, whereas EVA is preferred for its lightness and cushioning in both sports and casual footwear.

Some guidelines should be set to ensure that performance remains at an acceptable level. The following tentative values have been suggested. These can be compared with the microcellular rubber specification set out in Table 20, page 190.

Chapter-4

4.1 MY LABORATORY WORK

4.4.1. BONDING TEST:



1. SCOPE:

This method is intended to determine the peel strength of an

adhesive bond The method is applicable to all types of bonded joint where at least one of the adherends is flexible.

2. PRINCIPLE

Test specimens are cut from a bonded assembly which has been previously prepared, typically using the procedure described in:

- SATRA Test Method AM2- Solvent borne or water borne adhesive.
- SATRA Test Method AM M - Hot melt adhesives.

or other procedures such as factory prepared test specimens.

The test specimen is then peeled using a tensile testing machine while the forces required to separate the two adherends is measured and the type of bond failure is assessed.

3. REFERENCES

BS 1610 Part 1: 1992 - Specification for the grading of forces applied by materials testing machines.

SATRA test method AM2: 1992 - Preparation of water borne and solvent borne, bonded assemblies for peel tests.

SATRA test method AM 34: 1992 -Preparation of hot molt bonded assemblies for peel tests.

4. APPARATUS AND MATERIALS

4.1 A low inertia tensile testing machine with:

4.1.1 A means of continuously recording the force throughout the test.

4.1.2 A jaw separation rate of 100 ± 20 mm/mm.

4.1.3 The capability of measuring forces up to 500 N, to an accuracy

of 2% as specified by 'Grade 2' in BS 1610 Part 1: 1992, preferably with several lower force ranges for more sensitive measurements. For test specimens cut from direct vulcanized bonds, forces above 500 N may be necessary to peel the bond.

Suitable machines are available from SATRA reference numbers STM 161 and STM 466, together with a quick release type jaw. reference number STD 160 OR.

4.2 A cutting device such as a sharp knife or rotary disc cutler for cutting the test specimens from the bonded assemblies. This shall neither unduly compress nor force apart the layers of the test specimen at the edges during cutting and therefore a press knife is unsuitable.

4.3 A device for measuring lengths up to 70 mm to an accuracy of 0.5 mm. A steel rule or vernier calliper is suitable.

5. CUTTING OF TEST SPECIMENS

5.1 Between bonding and cutting the test specimens they should be stored in a standard controlled environment of $20 \pm 2^{\circ}\text{C}$ and $65 \pm 2\%$ rh for a minimum time of;

- 24 hours - hot melt bonded assemblies.
- 48 hours - all other types of bonded assemblies.

5.2 SATRA test method AM2 Method I (solvent borne and water borne adhesive)

The procedure in AM2 produces two bonded assemblies of width 70 mm and length 50 mm. For each bonded assembly, see Figure use the knife or circular cutter .

5.2.1. Cut an equal amount from the shorter edges of the assembly to produce an assembly of width 60 ± 1 mm.

5.2.2. Cut the remaining central portion in half to produce two test specimens of width 30.0 ± 0.5 mm and length approximately 50 mm.

The circular cutter may be capable of carrying out both operation in one pass.

5.3. SATRA test method AMI4 Method 1 (pre-coated materials)

The procedure in AM 14 Method I produces four bonded assemblies of width 70 mm and length 50 mm. For each bonded assembly use the knife or circular cutter to follow the procedure in sections 5.1.1 and 5.1.2.

5.4 SATRA test method AM 14 Method 2 (direct bonding)

The procedure in AM 14 Method 2 produces four bonded assemblies of width 20 mm and length 100 mm. These bonded assemblies require no further cutting. However, if the maximum jaw separation of tensile testing machine is less than . approximately 150 mm it may be necessary to shorten the unbonded tabs.

5.5 Non-standard sized bonded assemblies

If the bonded assemblies are less than the standard size use the knife or circular cutter to cut two individual test specimens of equal width, discarding marginal strips, approximately 5 mm wide on the 50 mm sides of the assembly.

6. PROCEDURE

6.1 If the test specimens were cut with a calibrated rotary disc cutter use the device to measure the width of each test specimen in millimeters, and record this value to the nearest 0.5 mm.

6.2 Optional Pre-treatments:

If required, conduct any pro-treatments at this stage. In the case of test specimens prepared by the procedure In SATRA test method AM 14 Method / 1 (pre-coated materials) ensure that the two test specimens cut from each assembly are subjected to the same pre-treatments before peeling. In all other cases where the toil specimen is to be subjected to a pro-treatment before being peeled, ensure that the two test specimens from an assembly are not allocated to the same pro-treatment nor both tested without a pre-treatment.

6.3 Adjust the tensile testing machine to an appropriate force range.

6.4. Firmly clamp one of the free ends of the test specimen into each of the jaws of the tensile testing machine.

6.5. Activate the continuous recording system and operate the tensile testing machine with a jaw separation rate of 100 ± 20 mm/min until either a bonded length of 30 mm has been peeled or one of the adherents tears through.

6.6. As the jaws separate' observe the type (s) of bond failure, see Figure 2 and Table I. This is particularly important in the case of cohesive failure as this can only be identifier during peeling.

6.7. On all separated lest specimen; estimate, where possible to the nearest 5% the percentage of the bonded area presented by each type of failure exhibited.

6.8. Study each force versus extension graph produced by the continuous recording system in section 6.6. If the force shows rapid fluctuations but the average appears to remain constant throughout the test, excluding any significant initial peak, see section 6.11, then

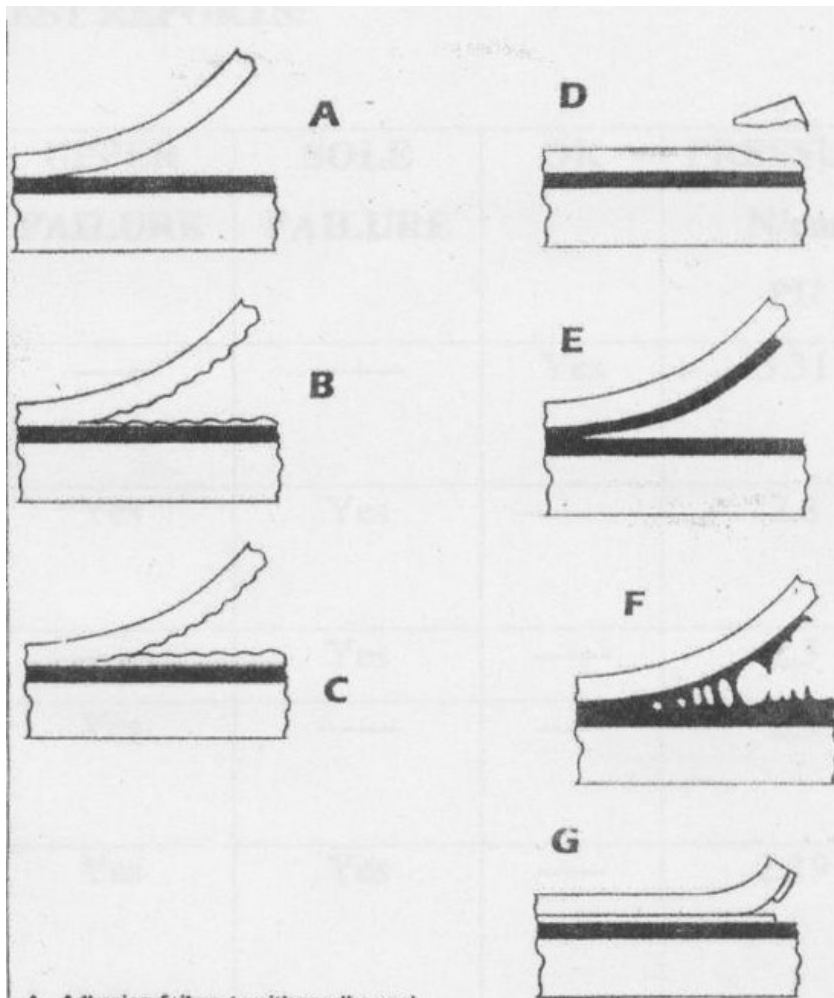
for each graph estimate the average peeling force, in newtons, see section-8.1 If failure is by tearing through either adherend with no subsequent peeling, measure the peak force.

6.9. For each test specimen divide the average peeling force (6.8) by the width of the specimen in millimeters, as measured in section 6.1, to give the average peel strength of each bond in N/mm, to the nearest 0.1 N/mm.

For test specimens cut from bonded assemblies prepared by the procedure in SATRA test method AM H Method 1 (pre-coated materials) calculate the arithmetic mean peel strength for the two test specimen cut from each of the four assemblies.

6.10. Calculate the arithmetic mean peel strength for those specimens or parts of specimens which show the same type of failure. Record the number of test specimens from which each result is derived, and the type of failure.

6.11. If there is a significant initial peak force on the graph, as shown in Figure, for example due to breaking of a surface layer, measure this value in newtons and divide it by the width of the test specimen in millimetres to give the initial peel strength of the bond in N/mm.



- A Adhesion failure to either adherend.
- B Surface failure of either adherend.
- C Deep failure of either adherend.
- D Tearing through either adherend.
- E Non-coalescence of adhesive film.
- F Cohesive failure.
- G Costing too high for the application.

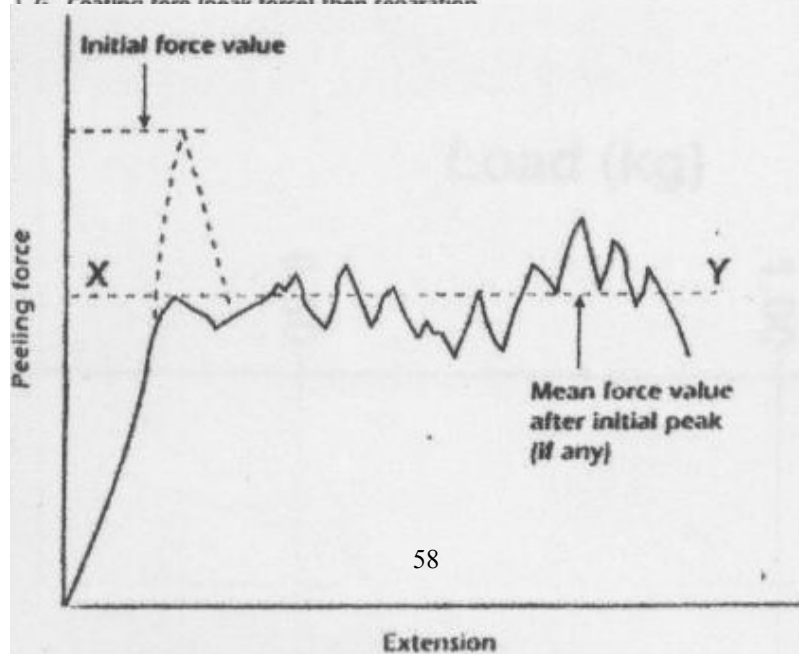


Figure: force extension peeling graph, including possible initial peak

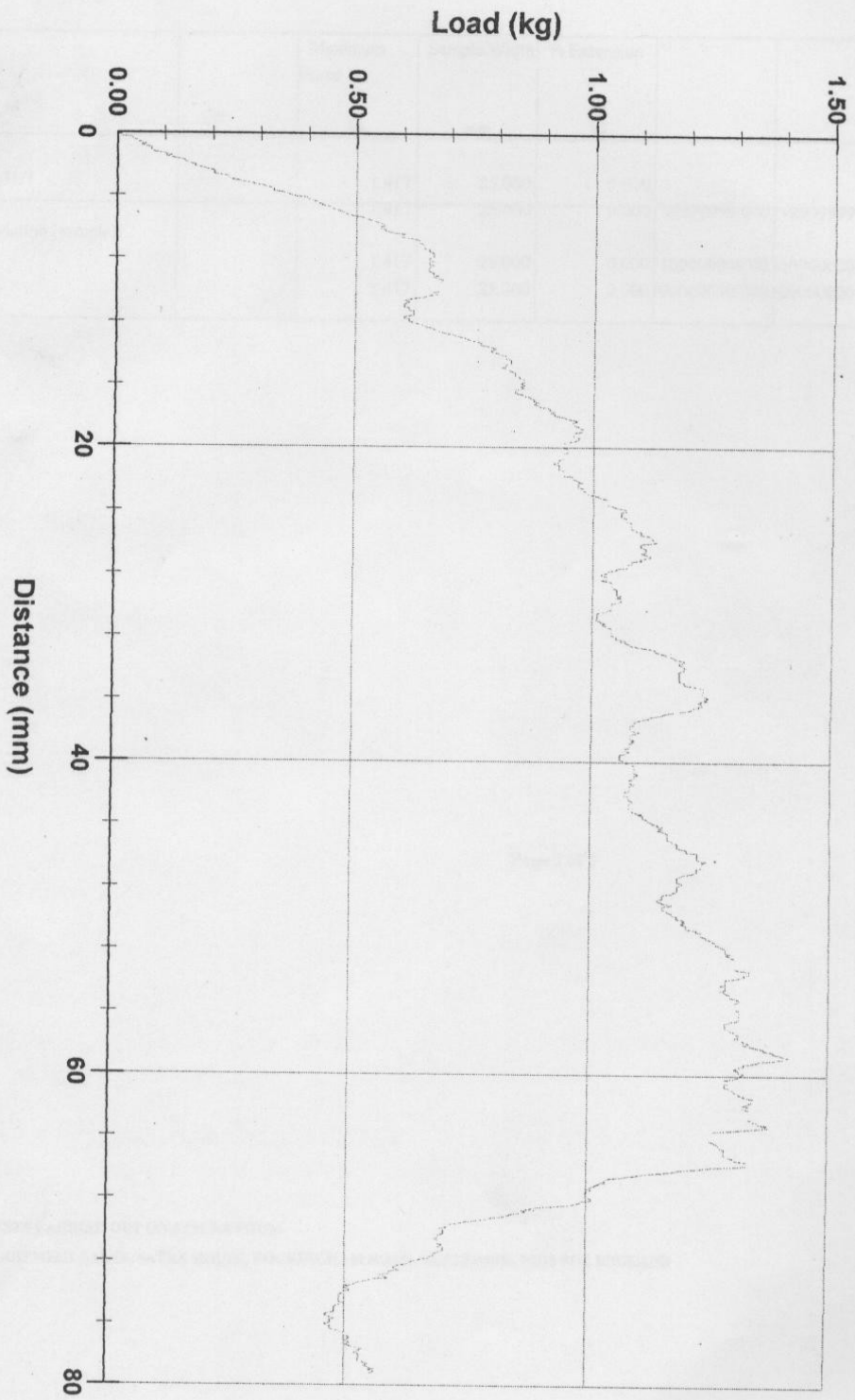
4.1.1.1 TEST REPORTS:

TYPES of Upper	UPPER FAILURE	SOLE FAILURE	OK	PRESSURE N/cm PU	PRESSURE N/cm Neoprene
Semi-Aniline	-----	-----	Yes	3.31	5.13
Corrected Grain	Yes	Yes	-----	2.8	5.01
Nubuck	-----	Yes	-----	2.3	3.74
Pigment Finish	Yes	-----	-----	2.5	3.45
PVC Coated Fabrics	Yes	Yes	-----	2.19	5.61
Mill Grain	-----	-----	Yes	2	2.54

: bolt

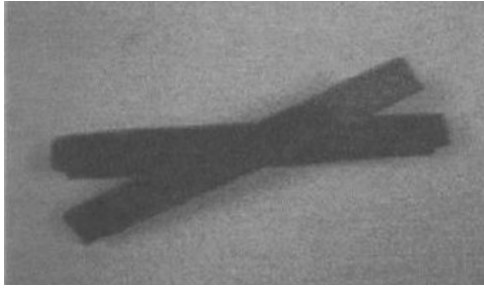
Split tear strength : sole-upper,1,31/1

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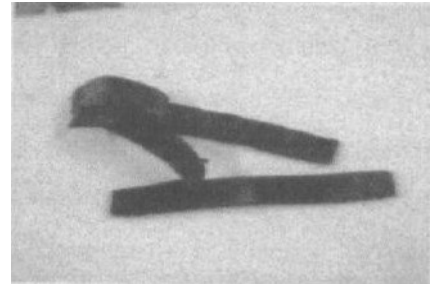


sole-upper,1,31/1

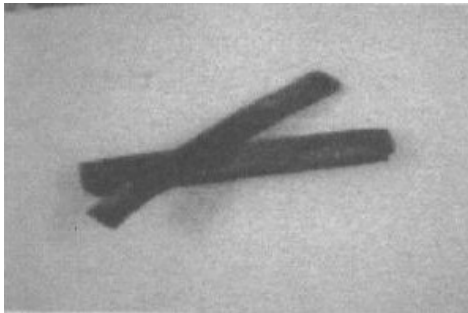
	Maximum Force	Sample Width	% Extension			
	kg	mm	%			
sole-upper, 1,31/1	1.417	25.000	0.000			
Mean	1.417	25.000	0.000	-9999999.000	-9999999.000	-99999
Standard Deviation (sample)						
Max	1.417	25.000	0.000	-100000000.00	-100000000.00	-10000
Min	1.417	25.000	0.000	100000000.000	100000000.000	100000



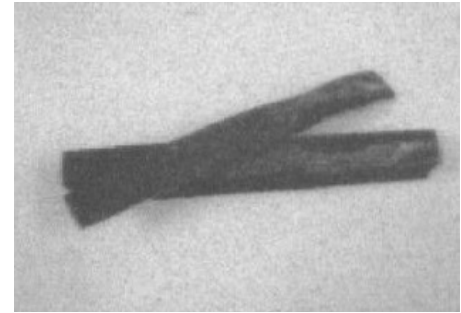
PVC Coated fabrics
Upper failure



Aniline finish leather
Sole and bond failure



Semi Aniline finish leather
Bond failure



Corrected grain leather
Bond failure

Figure: Tested Sample

8. Additional Notes:

8.1 Estimating the average peeling force on a force versus extension graph

The average peeling force can be estimated by visually comparing areas. When a horizontal line is drawn at the average peeling force (line XY in figure) the area bounded by the line and the curve above the line is equal to the area bounded by the line and curve below the line.

4.3.CONCLUTION

In my project-The standard value of Ethyl Vinyl Acetate sole bonding is 3N / cm under the standard pressure.

I have experimented on different types of leather at laboratory in Bangladesh College of Leather Technology.

I have found the satisfactory result from semi aniline finished leather and PVC coated fabrics to the standard value and the results were 5.13 & 5.61 N / cm respectively.

So we can say, EVA sole is suitable for semi aniline finished leather.

4.4. BIBLIOGRAPHY

1. World Footwear, vol. 07, No. 1, Jan/Feb, 1993
2. World Footwear, vol. 13, No. 4, Jul/Aug, 1999
3. World Footwear, vol. 14, No. 5, Sep/Oct, 2000
4. World Footwear, vol. 15, No. 1, Jan/Feb, 2001
5. World Footwear, vol. 15, No. 5, Sep/Oct, 2001
6. FDDI Footwear Digest, Issue. 24, Jan, 2000
7. FDDI Lasting Handouts, vol. I
8. SATRA Bulletin, Jan, 1995
9. SATRA Bulletin, Jun. 1999
10. SATRA Bulletin, Dec, 1999
11. Lecture Notes Provided by teachers.
12. Manual of Shoe Making by The Training Department CLARKS Limited.
13. Adhesive In Shoe Manufacture by B. Venkatappaiah
14. Footwear Materials And Process Technology by A.J. Harvey

