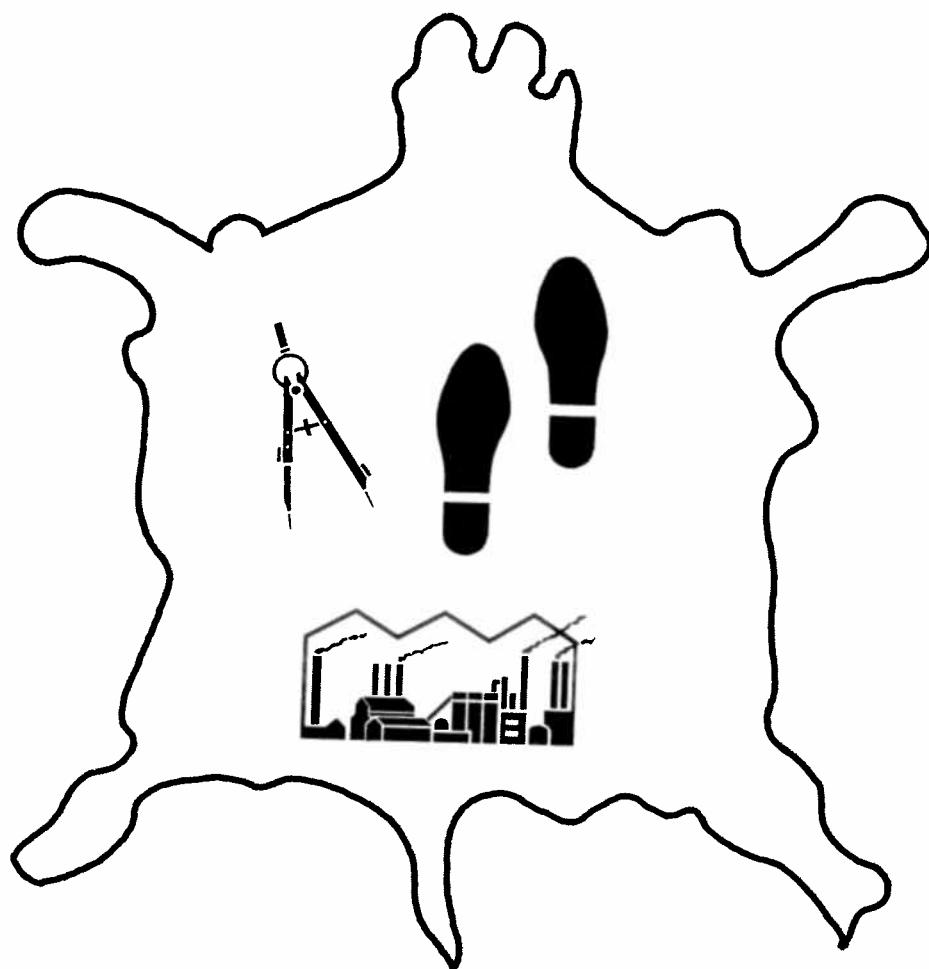


**SHOE INDUSTRY
DIPLOMA COURSE**



ADHESIVES*



*This document has been produced without formal editing



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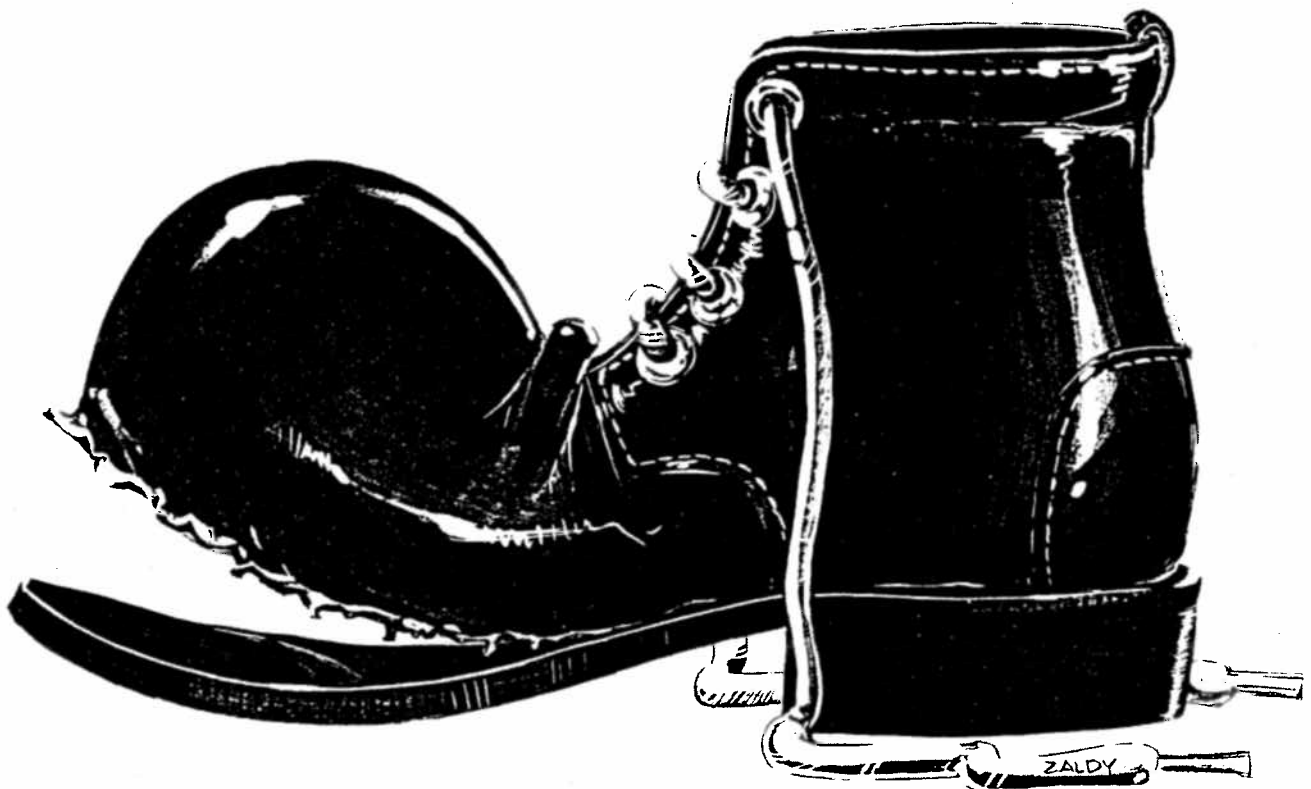
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- Pattern cutting
- Upper clicking
- Closing
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- Textiles and synthetic materials
- Elastomers and plastomers
- Purchasing and storing
- Quality determination and control
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- Adhesives
- Pattern making and engineering
- Shoe costing
- Grading

ADHESIVE



A D H E S I V E S

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A D H E S I V E S

An adhesives is a substance capable of holding materials together by surface attachment.

Adhesive is the general term and includes among other cement, glue, mucilage and paste. All of these terms are loosely used interchangeably

Adhesives have many uses in the industry and are an important auxiliary material. In bonding materials together, they are small in volume compared to other joining materials (metal, fibers, wood, etc.)

Among others the main advantages of adhesive bonding are:

1. Thin films, fibers, and small particles that could not be combined as well or at all by other techniques are readily bonded with adhesive (laminates, glasswool, fibers, abrasives, boards, non-woven, flocked fabrics, coating, etc.)
2. Stresses are distributed over wider areas.
3. The strength to weight ration and dimensional stability of anisotropic materials can be improved by cross-binding.
4. Adhesive lines provide insulation: electrical capacitors, circuits), moisture barrier, water vapor barrier, etc.
5. Dissimilar materials can be joined and lamination of such materials can give combination superior to either adherent alone.
6. Adhesive bonding may be faster and cheaper.

A. CLASSIFICATION OF ADHESIVES

Adhesives may be classified in many ways, e.g. by mode of application and setting, chemical composition, suitability for various adherents and end products, way of reaction, origine, etc.

For us, a convenient classification is based, first step, on the medium of the adhesive and on a second level on the origine. Though, in that classification, many adhesive having the same chemical composition will come in two or more categories.

1. Adhesives in water medium

- 1.1 animal origine : casein, hide glue, fish glue, white of eggs
- 1.2 vegetable origine: starch, flour, dextrine, glucose, vegetable resins, natural latex.
- 1.3 artificial or semi-synthetic origine: cellulose and wood derivatives, cellulose nitrate, methyl cellulose castor oil based polyurethanes.
- 1.4 synthetic origine: resins, ureum, formaldehyde, melamine, phenols, some acrylics, butadienes, PVC, PVA, etc.

Water medium adhesives have many utilizations, they are in solution or in emulsion and their residue is more or less water sensitive.

2. Adhesives in organic solvent

- 2.1 Rubber cements (dissolution) natural rubber, derived from the rubber latex, dissolved in solvents such as carbontetrachloride, trichlorethylene or benzene

2.2 Synthetic Rubbers Adhesives

- 2.2.1 polychloroprene adhesives
- 2.2.2 polyurethane adhesives
- 2.2.3 Butyl rubbers and polyisobutylene adhesives used as flocking adhesives, pressure sensitive adhesives and sealants
- 2.2.4 Nitrile rubber and acrylonitrile rubber adhesives used as laminating adhesives and sometimes in footwear for attaching oil resistant or vinyl rubber soles (Hycar Goodrich)
- 2.2.5 Styrene butadiene rubber adhesives (SBR) used as pressure sensitive adhesives
- 2.2.6 Thermoplastic rubber adhesives

2.3 Cellulosic Adhesives: nitrocellulosics

3. Solid Adhesives

- 3.1 Hotmelts : polyamides, polyesters, EVA
- 3.2 Resine Adhesives: epoxy and aminoresine adhesives

B. THE PRINCIPLES OF ADHESION

ZYGOLOGY is the science applied to the joining of materials. It includes the study of adhesion, welding, rivetting and all forms of mechanical jointing.

With footwear materials only two principles of zygoology are applicable

- specific adhesion
- mechanical adhesion

1. Specific Adhesion 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 reaction.

An example of this type of bond is the sticking of thermoplastic rubber soling. TR requires a chemical pre-treatment, halogenation, to make it compatible with a P.U. adhesive so that a chemical bond can be formed.

2. Mechanical Adhesion gives a physical bond in which the adhesive keys in to the fibers or structure of the material to be bonded. It can therefore, be done only with porous materials such as leather and fabrics. The adhesive flows into the surface structure of the material and when the solvent in the adhesive has evaporated, the adhesive is keyed in to the material. The joint made cannot be broken without physically breaking either the adhesive or the surface of the material.

The adhesive is commonly applied and securely anchored to both surfaces to be bonded. Enough adhesive must be on each surface so that, when the two surfaces are brought together, the adhesive joins form a strong bond.

The more porous the surface, the more adhesive must be applied to make sure that enough adhesive remains on the surface to form the bond.

Table 1. Price Index of Adhesive Components,
Pre-1973.
(Ratio to Price of Polyvinyl Acetate, per pound,
Dry Basis)

Price Index	Price Index
Synthetic Resins	Solvents, Plasticizers, Humectants, Waxes
Polyvinyl acetate 1.0	Heptane 0.15
Polyvinyl alcohol 1.6	Mineral spirits 0.17
Polyvinyl butyral 5	Toluene 0.15
PVC and copolymers 1.4	Acetone 0.3
Acrylics 1.9	Methylethyl ketone 0.5
Cyanoacrylates 400	Diocetyl phthalate 0.6
Anaerobics 100	Tricresyl phosphate 1.7
EVA 1.6	Glycerol 1.0
Polyethylene 0.9	Ethylene glycol 0.5
Poly(ethylene terephthalate) 5	Paraffin wax 0.3
Nylon 8	Fillers, Solid Additives
Phenol-Formaldehyde 0.7	Kaolin 0.05
Urea-formaldehyde 0.3	Bentonite 0.04
Melamine-formaldehyde 1.9	Whiting 0.10
Epoxy 1.9	Silica 0.1
Unsaturated polyester 0.9	Zinc oxide 0.8
Polyurethane 4	Magnesia (rubber grade) 1.1
Synthetic Rubbers	Curing Agents, Catalysts
SBR 1.0	TETA (triethylene tetramine) 2.3
Nitrile rubber 2.4	TEPA (tetraethylene pentamine) 3
Neoprene 2.5	Hexa (hexamethylene tetramine) 1
Reclaim 0.9	Phenylene diamine 5
Butyl 1.4	
Polysulfide 4	
Silicone 8	
Low Molecular Weight Resins	
Rosin 0.7	
Rosin esters 1.4	
Polyterpenes 1.7	
Petroleum resins 0.8	
Coumarone-indene 0.6	
Natural-derived Polymers	
Starch 0.25	
Dextrin 0.5	
Wheat flour 0.2	
Soya flour 0.4	
Animal glue 1.1	
Casein 3	
Polyamide from dimer acid 3	
Natural rubber 0.9	
Oleoresinous 0.5	
Inorganic	
Sodium silicate (dry basis) 0.5	

C. PROPERTIES OF ADHESIVES

1. Viscosity

The viscosity is defined as the ratio of the shear stress existing between laminae of moving fluid and the rate of shear between these laminae.

It is usually expressed in centipoises (cP). The international S.I. unit is the pascal second (Pa.s) The pascal second is equal to the dynamic viscosity of a homogenous fluid in which, two layers 1 meter apart, the top layer is moving parallel to the bottom layer at a velocity of 1m/s and a shearing stress of 1 Pa is required to maintain this motion.

$$1 \text{ poise } P = 0.1 \text{ Pa.s}$$

$$1 \text{ centipoise } cP = 0,001 \text{ Pa.s}$$

The viscosity is measured by a rotating viscosimeter (Brookfield or Feranti)

2. Tack is the characteristic of an adhesive which causes one surface coated with an adhesive to adhere to another on contact.
3. Plasticity is the property of adhesives that allows the material to be deformed continuously and permanently without rupture of the material.
4. Stringiness is the property of an adhesive that results in the formation of filaments or threads when adhesive transfer surfaces are separated.
5. Penetration is the entering of an adhesive into an adherend.

6. Coverage is the property of an adhesive which determines the extent to which an adhesive can be uniformly spread over an area to be bonded with a unit weight or volume of adhesive.
7. Drying Time is the period of time during which an adhesive on an adherend or an assembly is allowed to dry with or without the application of heat or pressure, or both.
8. Setting Time is the period of time during which an assembly is subjected to heat or pressure, or both to cure the adhesive.
9. Working time or pot life is the period of time during which an adhesive after mixing with catalyst, solvent or other compounding ingredients, remains suitable for use.
10. Storage life or Shelf life is the period of time during which a packaged adhesive can be stored under specified temperature conditions and remain suitable for use.
11. Reactivation Temperature is the temperature on which a dry film becomes tacky. Usually, the suppliers recommend a reactivation temperature, that should always be higher for a one-way activation than for a two-way, e.g. 80°C for one-way and 60°C for two-way.

D. SELECTION OF ADHESIVES

The main points to be considered when selecting adhesives for footwear manufacture are:

- cost
- strength
- suitability for use with shoe materials and
- in shoe processes
- general considerations

1. Cost

Cost is obviously an important factor in the selection of an adhesive but it should not be the only criterion of selection.

The initial cost is not the only cost that goes into the establishment of the real cost. Amount of adhesive which must be applied, the possibility of wastage as affected by pot life or shelf life, the dry residue and the labour and equipment costs involved in its use affect the real cost.

Most of all, loss due to poor performance in wear, can make a cheap adhesive very expensive.

2. Strength

The strength of the adhesive must be adequate for its task, not only initially, but for as long that the shoe is in wear and under all possible conditions of service.

3. Suitability for use with shoe materials

A variety of materials has to be stuck together in footwear production, the adhesive must be compatible physically and chemically with the materials. The selected adhesive must also be suitable to the process being used.

4. General considerations

- 4.1 Adhesive should preferably have a long shelf life
- 4.2 Adhesive should preferably be non-toxic and non-inflammable
- 4.3 The adhesive should not shrink or contract on drying. If the adhesive shrinks the material may wrinkle and if it is applied only to one surface and shrinks considerably the bond could be broken by the contraction of one surface.
- 4.4 It is an advantage if the adhesive can easily be removed if misapplied and if stains can be removed.
- 4.5 The adhesive should not cause discoloration or spoil the surface finish of the upper.
- 4.6 Versatility, allowing the use of one adhesive for more than one purpose, is an advantage in the simplification of purchasing, storage and instruction in the manner of usage.

E. ADHESIVES USED IN FOOTWEAR AND LEATHERGOODS

1, Natural Rubber Latex

Latex is tapped from the tree *HEVEA BRASILIENSIS* and contains about 35% solids. It is immediately ammoniated to prevent bacterial attack and coagulation. The field latex is an emulsion of rubber in water, it is concentrated to a total solid content of 62 - 72% by one of three processes: centrifuging, evaporating or creaming.

Evaporated latex is produced by heating at reduced pressure, the ammonia usually being replaced by fixed alkali with the assistance of small amount of metallic soap to assist stabilization. Evaporated latex is not used as such but is a raw material for adhesive manufacture.

Creamed latex is prepared with a fatty acid soap and a creaming agent. It is not used as adhesive.

Centrifuged latex constitutes the bulk of marketed material. There are four main types designated by letters as follows:

- i) HA high ammonia latex containing 0.70 - 0.75% W/w NH_3
- ii) LA - SPP low ammonia latex (Santobrite) containing 0.2% ammonia and 0.2% sodium pentachlorophenate
- iii) LA - BA low ammonia boric acid latex containing 0.2% ammonia, 0.2% boric acid and 0.04% lauric acid sometimes 0.01% sodium pentachlorophenate

- iv) LA - ZDC low ammonia zinc diethyl dithiocarbamate latex containing 0.2% ammonia, 0.15 ZDC and 0.2% lauric acid

The stabilizing system can give interactions with the other constituents of the adhesive.

Latex emulsions used in footwear are adjusted for viscosity and ageing

A typical formulation is;

Natural latex 60% dry residue	100 parts
Sodium ethylenediamine tetraacetate solution at 20%	2.5 parts
Antioxydant e.g. a polymerized trimethyl hydro-quinoline as 50% dispersion	0.5 parts

Latex emulsions can be grafted with methyl methacrylates to give the "HEVEAPLUS" polymer which may be compared to a comb where the natural rubber forms the backbone and short lengths of methacrylate the teeth.

2. Rubber cement or dissolution

Natural rubber as precipitated and dried latex (smoked sheets or white solid latex) or vulcanized rubber or reclaim rubber are dissolved in organic solvents such as carbon tetrachloride, trichlorethylene or benzine to give an adhesive.

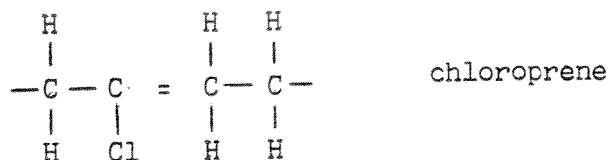
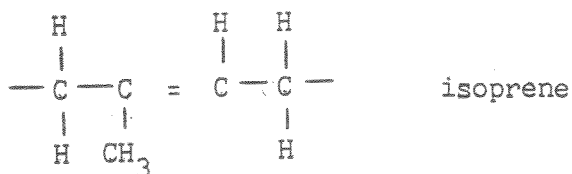
Those adhesives do not crystallize, remain wet for a long time, give a good adhesion but the bond is reversible and has a poor peel resistance.

3. Polychloroprene adhesives

Polychloroprene is the basis for one of the largest and most important group of rubber adhesives.

The rapid development of bond strength of films from solution, combined with tack or auto-adhesion as well as resistance of the cured adhesive line to heat, oxidation, water, solvents, oils, acids and alkalis, have led to the extensive use of polychloroprene adhesives in shoe, furniture, automotive and construction industries.

Neoprene was the first synthetic elastomers developed by Dupont de Nemours in the United States. It was discovered in the later part of 1920 and the first public announcement was made in 1931 and commercialization began in 1932. It was first known as "Duprene" and this polymer was designated NEOPRENE only in 1936. In the beginning, neoprene adhesives were much more expensive than the natural rubber cement (3-4\$ per gallon against 40-50 cts) and is is only during and after World War II, due to the shortage of natural rubber, that the use of polychloroprene became important. At the same time chlorinated butadiene rubber were developed in Germany, under the name of Perbunan and later on Baypren



Rapid bond strength development coupled with high ultimate strength has typified polychloroprene adhesives (fig. 1)

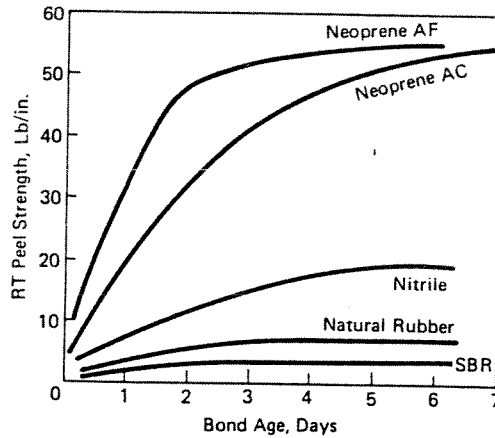


Fig. 1. Bond strength development: neoprene vs other elastomers.

3.1 Types of polychloroprene

The polymer structure of polychloroprene is determined by the manner in which the chloroprene monomer reacts with the polymer chain. Upon polymerization the chloroprene may take any of four isomeric forms (Table 2). The proportions of these configurations determine the amount of crystallization and reactivity towards vulcanization. Rapid bond strength development is associated with crystallization.

Table 2. Molecular Structure of Neoprene.

Type of Addition	Formula	Comments
<i>Trans</i> -1,4	$\begin{array}{c} \text{H} & & \text{H} \\ & & \\ \text{---C} & = & \text{C---} \\ & & \\ \text{H} & & \text{H} \\ & & \text{Cl} \end{array}$	increases crystallization
<i>Cis</i> -1,4	$\begin{array}{c} \text{H} & & \text{H} \\ & & \\ \text{---C} & = & \text{C---} \\ & & \\ \text{H} & & \text{H} \\ & & \text{Cl} \end{array}$	decreases crystallization
1,2	$\begin{array}{c} \text{H} & \text{Cl} \\ & \\ \text{---C} & \text{---C---} \\ & \\ \text{H} & \text{CH} \\ & \\ & \text{HCH} \end{array}$	active sites for vulcanization (decreases crystallization)
3,4	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{---C} & \text{---C---} \\ & \\ \text{H} & \text{C---Cl} \\ & \\ & \text{HCH} \end{array}$	decreases crystallization

Crystallization of a dry adhesive film is the property by which the long chains of molecules are displayed in such a way that intermolecular links appear. Crystallization is reversible and can be destroyed namely by heat.

Vulcanization is the linking of the long chains through an activator and is irreversible.

The crystallization rate influences the properties of the adhesive as shown in fig. 3

Crystallization Rate		Influence
medium	high	
—————→		Initial strength of bond
—————→		Rate of setting
—————→		Final strength of bond
—————→		Heat resistance of bond
←—————		Contact adhesion
←—————		Elasticity of bond

Table 3. Crystallization Rate

The viscosity of polychloroprene solutions depends also from the type of chloroprene and has an influence on the spreadability and on the wetting action on adherents (Table 4)

Solution viscosity		Influence
low	high	
←—————→		polychloroprene content at given viscosity
←—————		Spreadability of adhesive
←—————		Wetting action on adherents

Table 4. Solution Viscosity

3.2 Identification of Polychloroprene

Depending from the producer, the grades of polychloroprene are identified by letters (DU PONT) or by digits (Bayer)

Each grade of Baypren is identified by a three digit number.

The significances of the digits are as follows:

First digit	crystallization rate
2	medium
3	high
Second digit	solution viscosity
1	low
2	medium
3	high
4	very high
Third digit	indication of special properties

3.3 Production of Polychloroprene Adhesives

3.3.1 Polychloroprenes as raw material are in sheets or blocks, in chips or in granules. The sheets or blocks have to be cut into small pieces.

Despite their good degree of solubility, polychloroprenes must be masticated before dissolution in solvents.

Mastication depolymerizes the chain molecules of the rubber. It is performed on a mixing mill or in an internal mixer.

The heavy shear forces exerted on the material in these machines cause the long chain molecules to tear. The effectiveness of the shear forces is inversely proportional to the temperature of the material. If the rubber is relatively cool, the chain molecules are readily shortened by the vigorous milling or kneading action. At higher temperature the rubber becomes soft and plastic and therefore substantially escapes the shear forces through its ability to flow; the molecules, instead of being torn, tend to slide past one another.

The mastication machines have powerful motors. As the rubber absorbs energy, its temperature rises. The excess heat must be removed and the rolls of the mill must be cooled with water. Even so, the temperature of the rubber rises to about 60 to 80°C.

Before the beginning of mastication on mixing mill the rolls are set to a narrow gap of about 0.3 mm. After the chloroprene has been put through the mill 1 to 3 times a rough sheet is obtained. The sheet is passed between the rolls again. The front part of the sheet is cut with a knife and transferred to a tray to cool. Thereafter the material is returned to the mill and run off onto the tray until the required degree of depolymerization has been reached.

The amount of chloroprene that can be masticated as one batch depends on the dimensions, peripheral speed and friction ratio of the rolls.

During the mastication fillers and metal oxides are incorporated into the sheet.

3.3.2 Incorporation of metal oxides, fillers and resins

Most adhesive compositions contain metal oxides fillers and resins. These are added at the end of the mastication. For this purpose the gap between the rolls is increased to about 0.6 mm.

It is important to add the metal oxides and fillers at the correct time as soon as chloroprene has been sufficiently masticated, this is when the holes in the sheet disappear. Metal oxides and fillers must be added in the correct order to avoid interactions.

3.3.2.1 Role of the metallic oxides

The metallic oxides generally included in polychloroprene adhesives are magnesium oxide and zinc oxide.

Magnesium oxide effectively counteracts the scorching (burning) that can occur while the mastication is in progress.

Zinc oxide has a tendency to crosslink the chloroprene and therefore is added as the final ingredient of the batch.

By acting as acceptors for the traces of hydrogen chloride that are split off in the course of time by the polychloroprene, the two oxides improve the stability of the adhesive and increase the durability of the joints produced with it.

Magnesium oxide and zinc oxide are used in proportion of about 4% each calculated on the weight of chloroprene. Sometimes the oxides are replaced by carbonates to give more transparent adhesives.

Despite the presence of metallic oxides, it is important to package the adhesives in containers that are not attacked by hydrochloric acid. The plating of tinfoil must be without defects and sufficiently thick, otherwise iron chloride may form on the walls of the container. This compound reacts with other components in the adhesive.

3.3.2.2 Role of Fillers

Fillers of many different kind can be used in adhesives, the proportion depending on the purpose for which the adhesive is intended. Fillers are kaolin, whiting, barytes, quartz flour, asbestos flour, carbon black and silica.

Adhesives containing fillers have good gap-filling effects, but fillers can have an influence on the strength of the bond. Silica are good in adhesives used to bond stiff materials, they increase the initial strength of the bonds and accelerate their setting, they also increase slightly the heat resistance of the bond.

If the adhesive is required to be of a particular color, pigments can be incorporated in the same way as fillers.

3.3.2.3 Role of Resins

The properties and adhesive effects can be improved very much with suitable resins.

Additions of resins enable the open time to be varied greatly

- reduce the setting time
- affect the crystallization
- influence the hardness and brittleness of the film
- allow the heat-activation to various extent
- modify the viscosity

Numerous natural and synthetic resins are compatible with polychloroprene solutions, such as resins, phenolics, terpene and coumarone resins.

3.3.3 Solvents

Polychloroprenes are soluble in many organic solvents and mixtures of organic solvents.

Apart from the dissolving action, the main factors which governs the choice of solvents or solvents mixtures are:

- The effects on the technical properties of the adhesive
 - viscosity
 - drying and setting time
 - open time
 - gelling
- considerations of industrial hygiene and fire safety
- economic considerations

For an organic solvent to dissolve polychloroprene it is necessary for the molecules of the solvent to overcome the physical forces active between the polychloroprene chains.

The solubility of polychloroprenes depends thus on the properties of the chosen solvent. Each solvent has a solubility parameter designed by the greek letter δ and is composed of three vectors:

- δ_d the dispersion force
- δ_p the polar intermolecular forces; and
- δ_h the hydrogen bonding

There are thus for each type of chloroprene, true solvents and solvents without dissolving action. The latter can be used as dilutants. Because of the specific dissolving action care should be taken, when solvents are added to adhesives.

Table 5 give some examples of solubility, effect on open time and effect on viscosity.

TABLE 5

SOLUBILITY OF POLYCHLOROPRENE
(type x)

<u>one solvent</u>		<u>mixture of 2 solvents</u>			
Acetone	insoluble	Methylacetate + MEK	2 : 8	insoluble	
Methyl ethyl Ketone MEK	soluble	Ethylacetate + MEK	1 : 9	soluble	
Methyl acetate	insoluble		9 : 1	swells	
Ethyl acetate	swells		8 : 2	soluble	
But yl acetate	soluble	Acetone + MEK	2 : 8	insoluble	
Petroleum spi. n-Hexane	insoluble		1 : 9	swells	
Trichlorethylene	soluble	Petroleum sp. + MEK	7 : 3	insoluble	
Toluene	soluble		6 : 4	soluble	
		Methyl acetate + Toluene	8 : 2	insoluble	
			7 : 3	soluble	
		Acetone + toluene	7 : 3	insoluble	
			6 : 4	soluble	

mixtures of 3 solvents

Methyl acetate + Toluene + Trichloro ethylene	8 : 1.5 : 0.5	insoluble
Ethylacetate + toluene + Trichloroethylene	8 : 1.5 : 0.5	soluble
Petroleum + toluene + Trichloroethylene	8 : 1.5 + 0.5	insoluble
Methyl acetate + petroleum + toluene	3 : 6 : 1	insoluble
	2 : 7 : 1	insoluble
	4 : 4 : 2	soluble
	3 : 5 : 2	soluble
	2 : 6 : 2	insoluble
	1 : 7 : 2	insoluble
	1 : 6 : 3	insoluble

mixture of 3 non solvents

Methyl acetate + acetone + petroleum spirit	1 : 1 : 1	soluble
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TABLE 6

INFLUENCE OF SOLVENT ON VISCOSITY

20% Polychloroprene x

SOLVENT	SOLVENT RATIO p.b.w.	VISCOSITY Pa.s
Trichloroethylene		27.3
Toluene		2.8 *
Toluene + hexane	6 : 4	1.7
Ethyl acetate + Hexane + toluene	2 : 2 : 1	0.9
Ethyl acetate + Hexane + MEK	3 : 5 : 2	0.5
Cyclohexane + Hexane + MEK	1 : 1 : 1	0.6
Cyclohexane + Hexane + MEK	2 : 1 : 1	0.6

TABLE 7

ADHESIVE WITHOUT RESIN

SOLVENT	SOLVENT RATIO p.b.w.	OPEN TIME (min)	
		Storage time	
		1 day	6 months
Toluene		150	150
Methylene chloride		20	20
Trichloroethylene		20	60
Methyl ethyl ketone		60	120
Toluene + petroleum spirit	2 : 1	100	100
Toluene + petroleum spirit	3 : 2	90	90
Toluene + petroleum spirit	1 : 1	60	90

TABLE 8

INFLUENCE OF SOLVENT ON SETTING

Adhesive without resin

SOLVENT	SOLVENT RATIO (p.b.w.)	at once	Peeling resistance (N/mm) determined after bonding					
			1 h	2 h	4 h	6 h	1 d	9 d
Toluene		0.7	0.3	0.2	0.4	0.4	6.7	8.8
Methylene chloride		1.7	1.0	1.0	1.7	3.2	7.1	8.4
Trichloroethylene		0.9	0.5	0.4	0.7	0.7	5.8	8.9
Methyl ethyl ketone		1.2	0.6	1.5	5.5	8.0	8.1	9.8
Toluene + petroleum spirit	2 : 1	0.6	0.3	0.3	0.5	0.7	7.7	8.6
Toluene + petroleum spirit	3 : 2	0.7	0.4	0.4	0.7	1.4	7.2	8.5
Toluene + petroleum spirit	1 : 1	1.1	0.5	0.5	0.9	2.9	7.0	7.8
Toluene + methyl acetate	2 : 1	0.7	0.3	0.3	0.5	0.8	7.3	10.0
Toluene + methyl acetate	2 : 3	0.9	0.5	0.5	1.6	4.5	6.7	8.1
Toluene + methyl acetate	3 : 7	1.2	1.1	1.7	6.7	7.2	8.2	9.4
Toluene + ethyl acetate	2 : 1	0.8	0.3	0.3	0.6	0.8	5.5	6.0
Toluene + ethyl acetate	1 : 2	1.0	0.6	0.3	0.5	1.1	6.2	6.5
Toluene + ethyl acetate	1 : 4	0.8	1.3	3.3	6.3	7.5	8.5	10.5
Toluene + ethyl acetate	1 : 8	1.1	2.4	2.7	3.4	3.6	3.8	3.4
Toluene + acetone	2 : 1	0.7	0.3	0.3	0.4	0.6	7.0	9.5
Toluene + acetone	2 : 3	0.9	0.6	0.6	1.7	5.6	7.7	9.6

4. Polyurethane adhesives

The use of polyurethane adhesive is recent (1960). Their use is increasing because of their exceptional properties. In footwear, they were restricted to materials difficult to bond. Indeed, they show a high resistance to plasticizers of PVC, to oils and to fat. Like polychloroprenes, they are thermoplastic and crystallize, but in addition their particles are smaller and more reactive so that penetration and fixation in the adherents are stronger. They also can give reactions in situ.

There are many types of polyurethane and many ways of application.

Isocyanates are the base of P.U. adhesives together with the reaction compounds isocyanates with polyesters or polyethers.

Isocyanates have:

- a high reactivity
- can undergo self polymerization
- are quite soluble in many organic substances and
- due to their small molecular size readily penetrate porous structures
- the reaction of isocyanates with polyethers and polyesters produce strong, polar, flexible P.U. which when wet, penetrate and show strong attraction for many substances

Isocyanates can be used as primer to bond two elastomers or they can be mixed with an elastomer.

Polyisocyanates can be mixed with other material and the combination is pre-reacted or allowed to react in situ.

Polyurethane can be used with or without polyisocyanates

Polyisocyanates can be blocked in aqueous suspension or in solution applied on adherents and reactivated in situ.

Polyurethanes can be made in aqueous suspensions or emulsions, in films or tapes and in powder.

The early difficulties of instability and poor hydrolysis resistance are now completely overcome.

At the present time, the polyurethane adhesives used in footwear are mostly of the polyester type. They have high uniformity and stability, they are easy to produce and adhere excellent to a wide range of materials because of the polarity of the polyurethanes and their ability to participate in the formation of hydrogen bridge bonds. (specific adhesion)

There are different grades of polyester P.U. All of them are soluble in ketones (e.g. acetone and MEK) and most are soluble in esters (acetates) and chlorinated hydrocarbons.

The main reasons for the success of P.U adhesives are:

- simplicity of production and processing
- good adhesion on many different materials
- high strength and ageing resistance of the bonds
- excellent resistance of the bonds to plasticizers

Adhesives based on polyurethane with low rates of crystallization have only a short open time and are therefore used by heat activation method. P.U. based adhesive are used mainly for two parts adhesive systems because the addition of the activator improves the adhesion to many materials and raises the heat resistance of the bonds.

5. Nitrocellulose Adhesives

Are made from nitrocellulose dissolved in strong solvent of the ketone group. They were the first synthetic adhesives used in footwear industry and have been replaced by polychloroprene and polyurethane.

Nitrocellulosic adhesives had to be compounded with plasticizers to give flexible film. On ageing, the plasticizers show a tendency to migrate in the adherents and as a result the bond becomes brittle.

6. Hot melts adhesives

These are solid adhesives. The raw material is no more a rubber like compound but a plastic. They are based on polyesters or polyamides and to a lesser extent on EVA or PU.

They are delivered in rods, granules or films and melted by heat for application and bonding.

Polyesters need a higher temperature to melt than polyamides, 190°C softening point for polyesters against 170°C for polyamides.

These adhesives are used for:

- lasting
- binding and folding
- lining and upper part bonding
- laminating

Their advantages are mainly their resistance to water, organic solvents, oils, and fats, acids and alkalis, they are easy to apply, but have a very short open time (more or less 3 seconds) and become brittle during ageing. They are without solvent and have a very short setting time, but need machines for their application and do not penetrate in the materials.

The injection temperature or melt pot temperature is always higher than the softening point and is given by the producer of hot melts. Generally it ranges between 230 and 240°C for polyesters and 180 to 200°C for polyamides.

Polyesters are only recommended for toe and seat lasting because of their poor flex resistance. Polyamides have a much greater resistance to flexion.

It is important that machines should not be left "ON" for long periods without being used; continuous re-heating of the adhesive will cause it to degrade. Sporadic use for short time of hot melt equipped machines will also cause degradation of the adhesive in the melt pot.

HOT MELT (polyester type)

Melt viscosity at 200°C	Pa.s	29	53
at 220°C		20	33
Melting Temperature		178°C	
Flow Temperature		180 - 182	
Recrystallization Temperature		± 112	
Processing Temperature		210 - 220	
Temperature in feeding hoses and injection nozzles		200 - 210	
Extreme Temperature		280	

7. Two components adhesive systems

Polychloroprene and polyurethane adhesives can be used in two component system, also called self-vulcanizing system, in which a vulcanizing agent or activator or curing agent is added to the adhesive solution. That agent is a polyisocyanate which will react with the adhesive molecule to initiate a reticulation similar to the vulcanization process, but without the help of heat.

Such "two component" adhesive systems are widely used when strong bonding and high heat resistance are required.

There is a variety of polyisocyanates with or without solvent. The grades that contain solvent differ from one another in isocyanate content (% of NCO groups), type of solvent and color (Table)

Types of isocyanates - Bayer Desmodur in solution

Grade	NCO Content %	Concentration of solution	Solvent	Color
Desmodur R	7.0	20 %	methylene chloride	green to violet
Desmodur RF	5.4	20 %	methylene chloride	yellowish brown
Desmodur RC	7.0	30 %	ethyl acetate	yellowish
Desmodur L 75	13.0	75 %	ethyl acetate	bright yellow
Desmodur KN	1.7	70 %	ethyl acetate	bright yellow

Two components systems are easy to prepare, however, some precaution have to be taken:

- as soon the isocyanate comes in contact with the adhesive, the reaction of reticulation starts. The two component must be mixed under strong agitation and the mixture has a short pot-life, it should be prepared immediately before application and used during the first hours following preparation (6 hours)
- the adhesive films on the adherents have also a short life and adherents may not be stored for a long time.
- some adhesive have resins that can react with the isocyanates and are not compatible with the activator
- the proportions of the mixture must be exactly followed: volume or weight of adhesive and volume or weight of isocyanate. Because of the presence of solvent, volume measuring is faster than weighing.

- the mixture must be homogenous. When the isocyanate is colored, this is easy to observe if the mixture is made in a glass container.
- residues of adhesive should be thrown away and the mixture always prepared in clean containers.
- brushes should be thoroughly cleaned at the end of each day.
- isocyanates are sensitive to humidity, this can cause problems in countries, like the Philippines.

F. APPLICATION OF ADHESIVES

All the aspects of application of adhesives and bonding of materials in construction of footwear are extensively discussed in the technology course and experience is acquired in the practical part of the course.

The following paragraphs will cover some reminders and new developments.

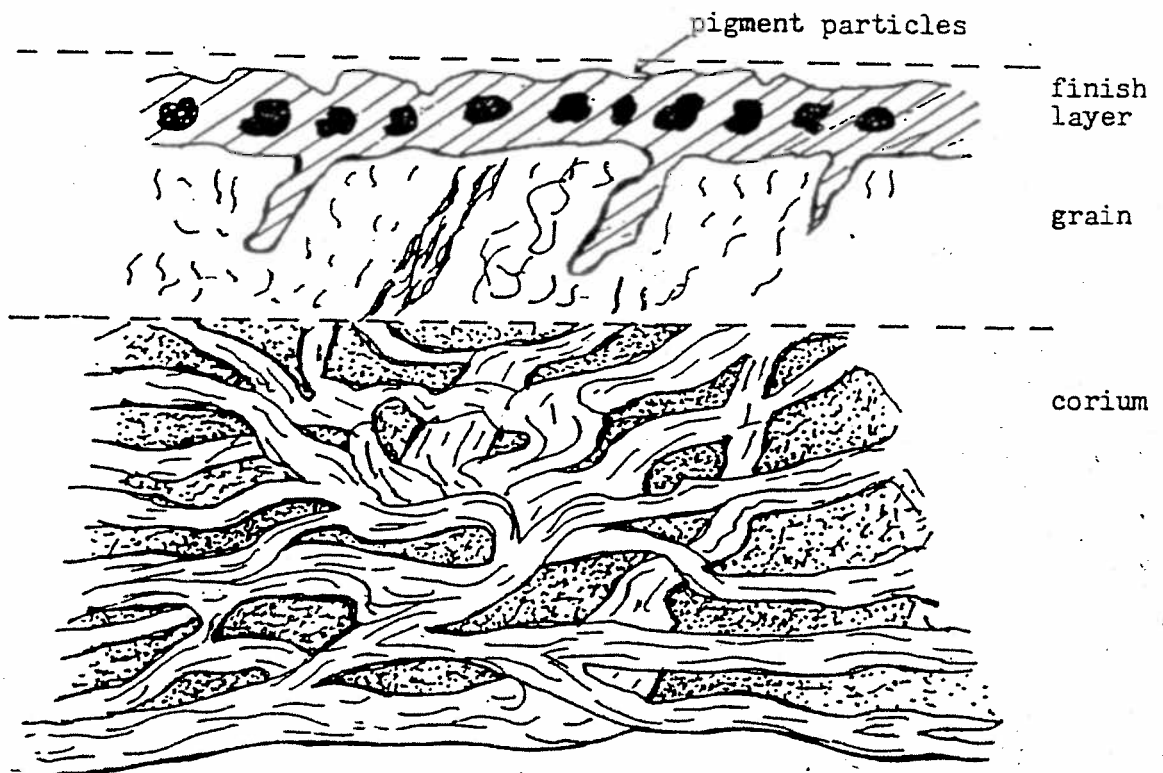
1. Surface Preparation

There are three ways for surface preparation:

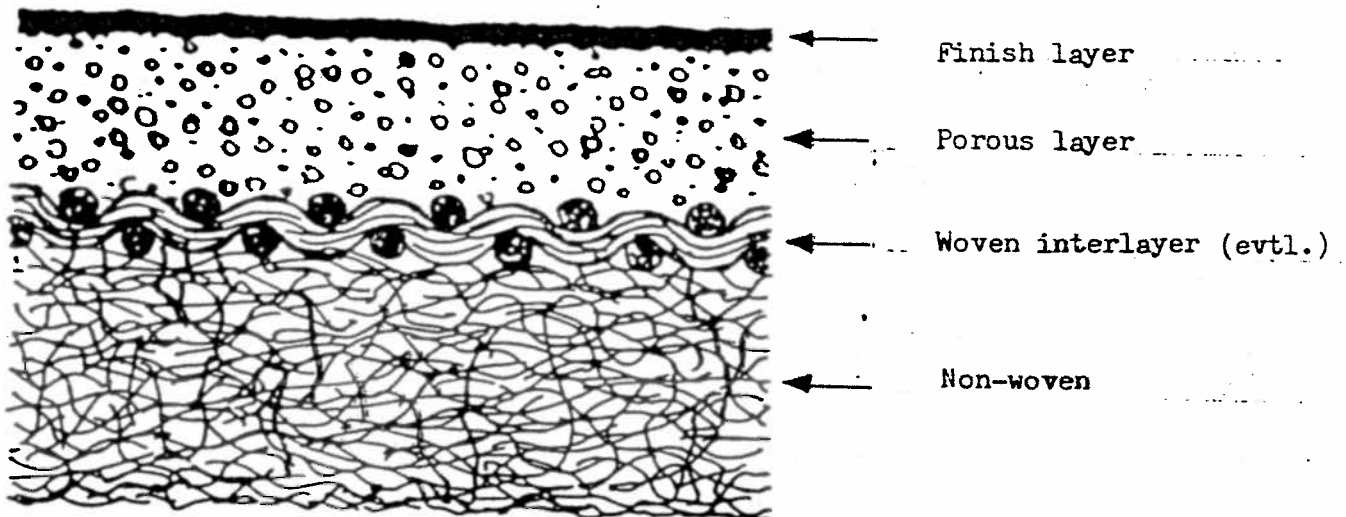
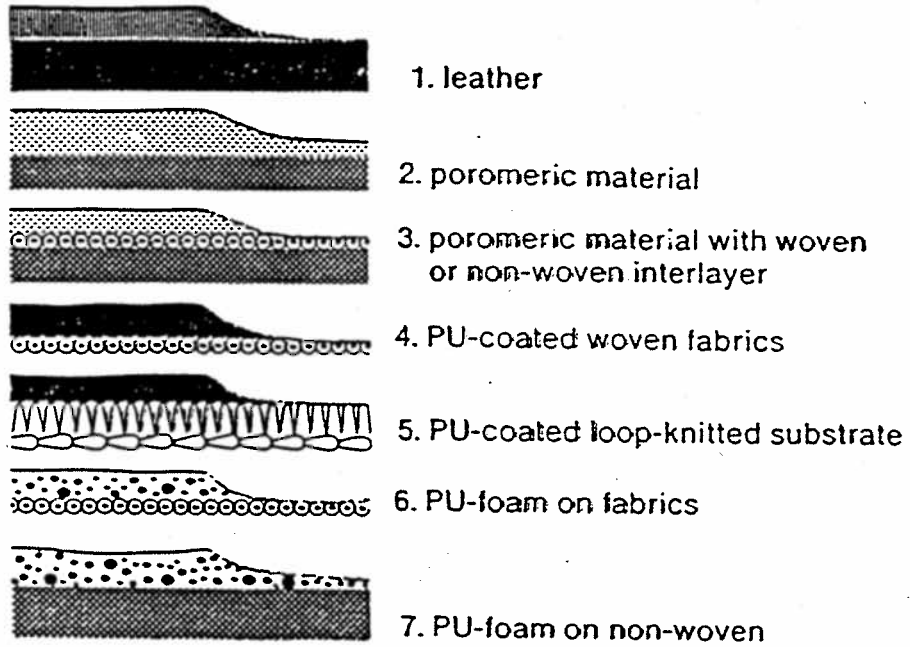
- a) mechanical : roughing, scouring, splitting
- b) chemical : wiping and cleaning with a organic solvent
- c) halogenation or chlorination

1.1 Mechanical

Taking into account the structure of the cross section of the upper materials - leather, poromerics, coated fabrics - roughing should always go up to the strongest part of the structure (see fig.)



Roughing of different types of upper materials
roughing plane



Type of Poromeric

Mechanical preparation of leather soling materials should eliminate all the loose fibers from the flesh side.

For other soling materials, elastomeres or rubber like materials, surface preparation is not intended for removing a weak part of the structure, but for elimination of the oxidized surface and of the migrated fatty components of the material. As the elastomeres will further oxidize, and the fatty components will further migrate, surface preparation must be done immediately before adhesive application.

1.2 Chemical

This seems the easy way of preparation, in fact, it is the most difficult and most of the time it becomes a dilution and repartition of fat and plasticizers instead of their elimination.

It is of utmost importance that cloth and solvent should always be clean. Chemical preparation must also occur immediately before adhesive application.

1.3 Halogenation or chlorination

When thermoplastic rubbers (TR) came on the market, the shoe manufacturers had very big difficulties to bond TR soles to any kind of the upper materials.

TR rubbers are based on butadiene styrene synthetic rubbers, but are not vulcanised like other natural or synthetic rubbers, they can be injected in molds. The process of making TR soles is much easier than the traditional vulcanization process.

The traditional methods of preparation give bad results on TR rubbers; roughing is creating heat in the material and the beginning of softening, chemical cleaning is insufficient and splitting gives only a physical change of the surface, further splitting is not possible on unit soles.

The only possibility to make TR compatible with adhesive is a strong oxidation and attack of the outer layer, and at the same time the fixation of chemical radicals on the TR, those radicals will give permanency to the treatment, which is a kind of re-vulcanization.

Halogens met all the requirements, but their application is not easy, only one of them, bromine, is a liquid. It gave very good results, unfortunately that chemical had to be abandoned because of health hazards. Chlorine is a gas, existing also in salts, it can be dissolved into water in limited concentrations (Chlorox). Researchers succeeded to prepare stronger solutions like Satreat from Satra England which is a mixture of organic solvents that can liberate Chlorine or Tenosol from TNO Holland which is a strong solution of chlorine or Lacnol. (South Africa) which is a solvent acid mixture.

Halogenation can also be applied to other rubber or rubberlike soling materials. However, because the presence of fats or mould lubricants it is advisable to split, rough or wipe those materials before halogenation. It is also advisable to use only PU adhesives on halogenated materials.

Halogenation is widely applied on unit soles with raised welts which are difficult to rough.

After halogenation the soling materials need to be thoroughly dried, this takes a long time (45 min to 1 hour depending from the liquid medium and the drier).

The halogenation liquids have a short life, they are destroyed by humidity and U.V. and their activity must be checked. They also react with metals so that they may not be used in metallic containers or with brushes having metallic parts.

They are also two components halogenation products which can be prepared immediately before utilization. The prepared solution has a pot-life of a few days.

2. Method of Application

2.1 Application of liquid adhesives

The various types of equipment used to apply adhesive can be summarized as follows:

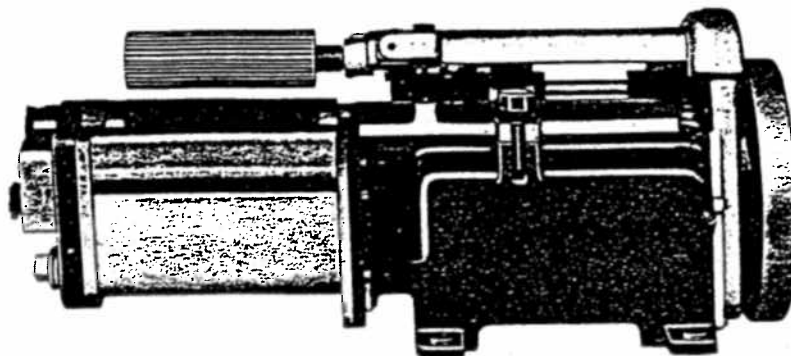
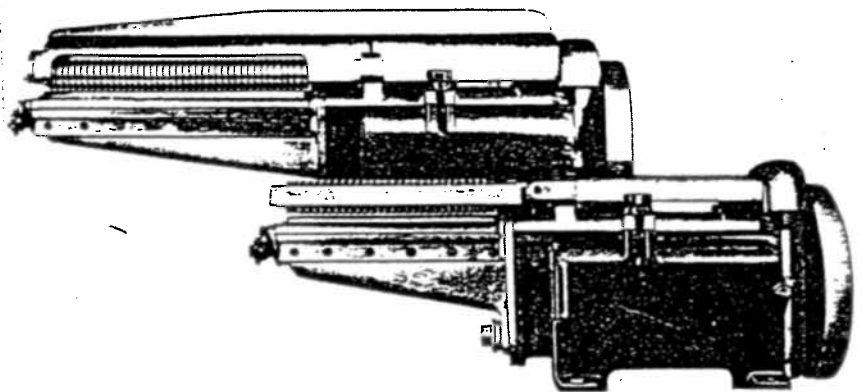
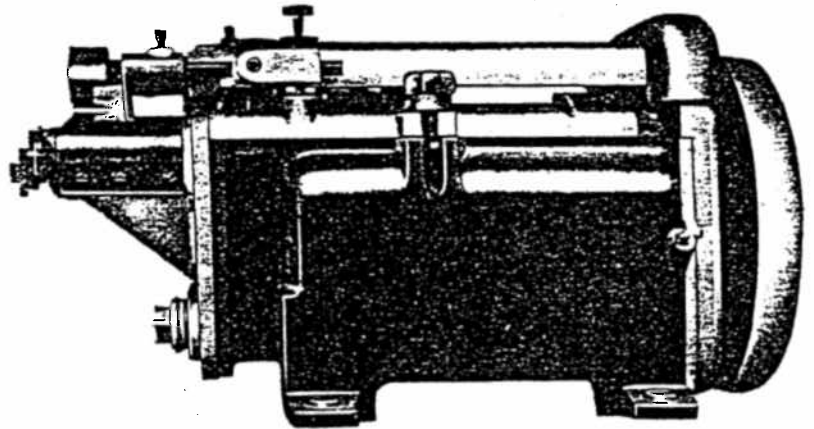
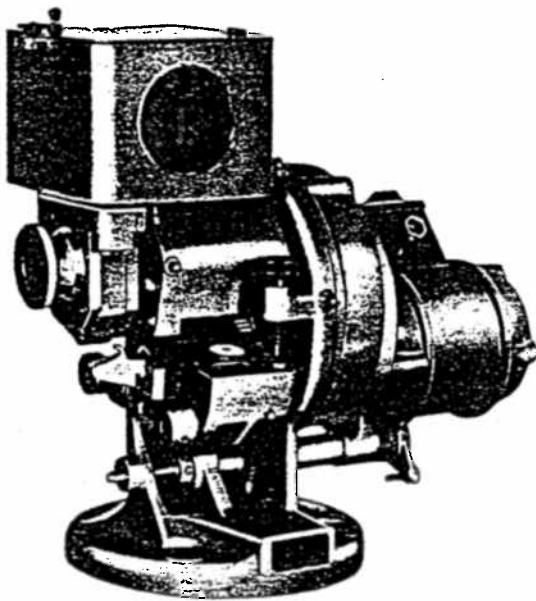
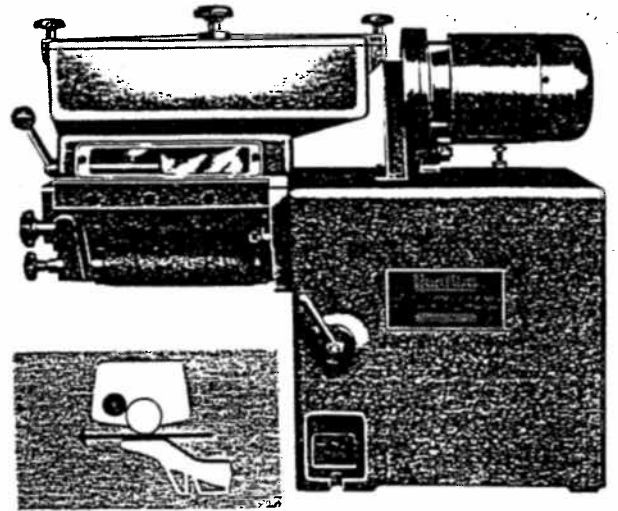
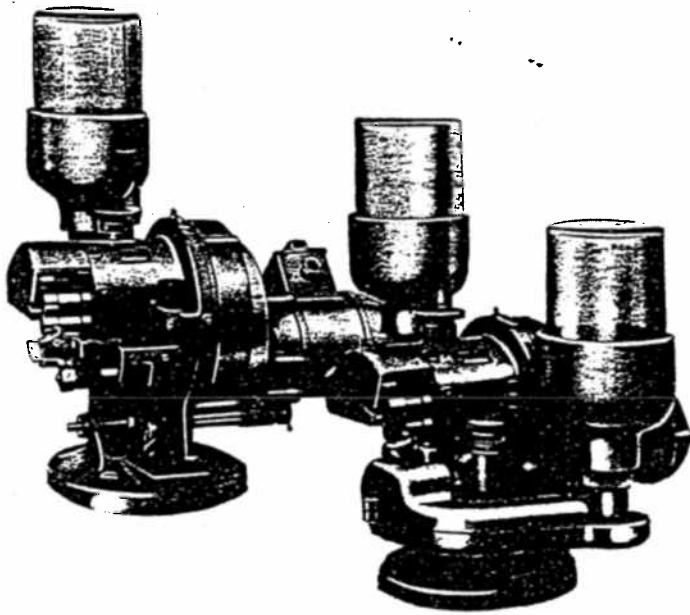
- hand brush
- hand dispenser
- brush feeded thru a pipe by a compressed air operated adhesive dispenser
- spraying gun (mostly for latex)
- adhesive applying machine using gravity (for low viscosity adhesives such as latex)
- adhesive applying machine using pumping systems based on different principles (high viscosity adhesive)

Some machines are designed to apply cement over the whole surface or over the components edge only. Some will apply adhesive in dots only for backing.

The adhesive selection has to be based on the equipment capacity and suitability. A machine suitable for latex will not work with polychloroprene, therefore, in case of doubt one shall not hesitate to consult the machine supplier. When using dispensers or machines to apply adhesives it is necessary to make sure that the viscosity of the adhesive is adequate.

Also cleaning of the machines is of great importance and to insure its cleanliness, cleaning of the machine has to be done with the adequate solvent.

ADHESIVE APPLYING MACHINES



REMINDERS

Amount of adhesive should be such that an even and continuous film is present on the adherents.

All porous materials should have two layers of adhesive, one penetrating in the material, the other covering the material.

Viscosity is not always related with dry residue.

Solvent

Organic solvents are the vehicle allowing to apply the adhesive and, to a certain extent, the penetration in the adherent.

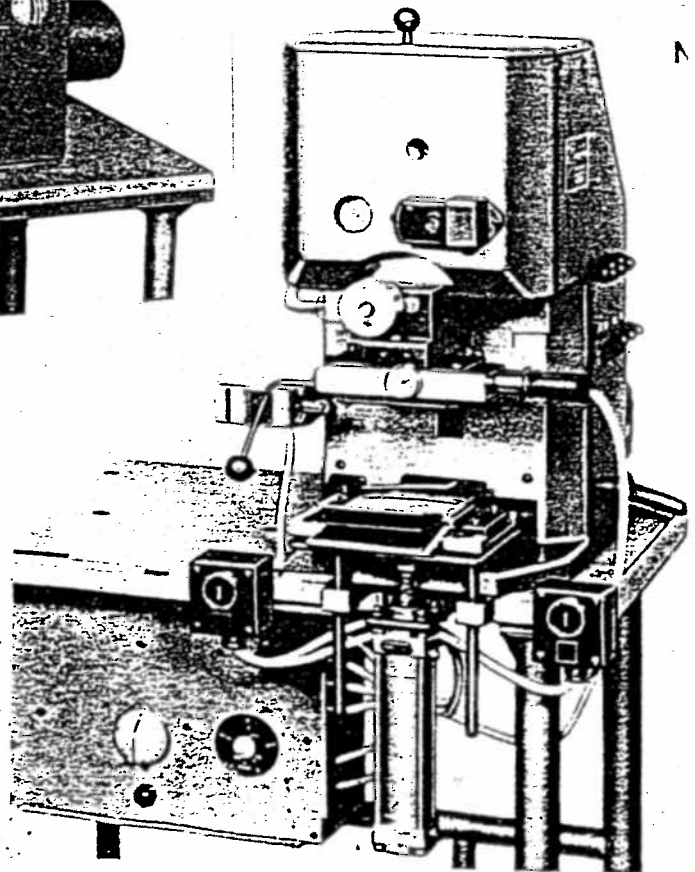
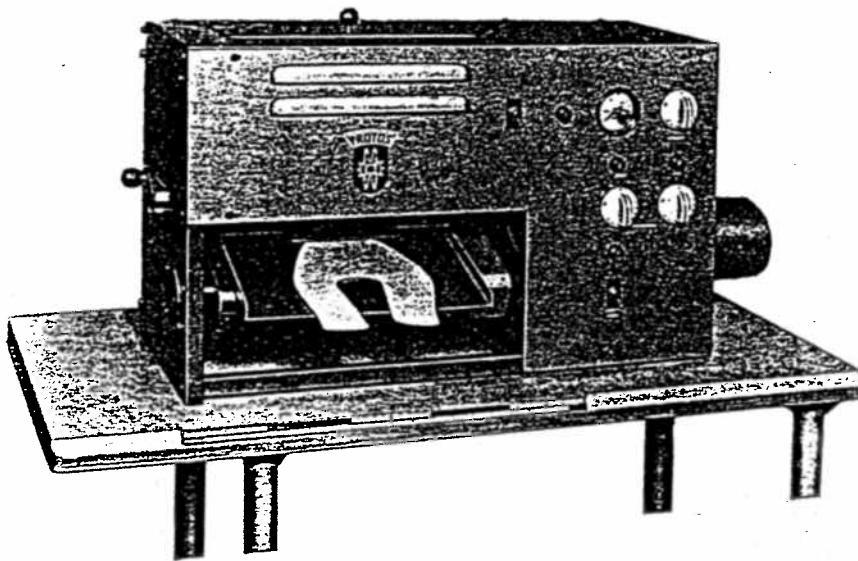
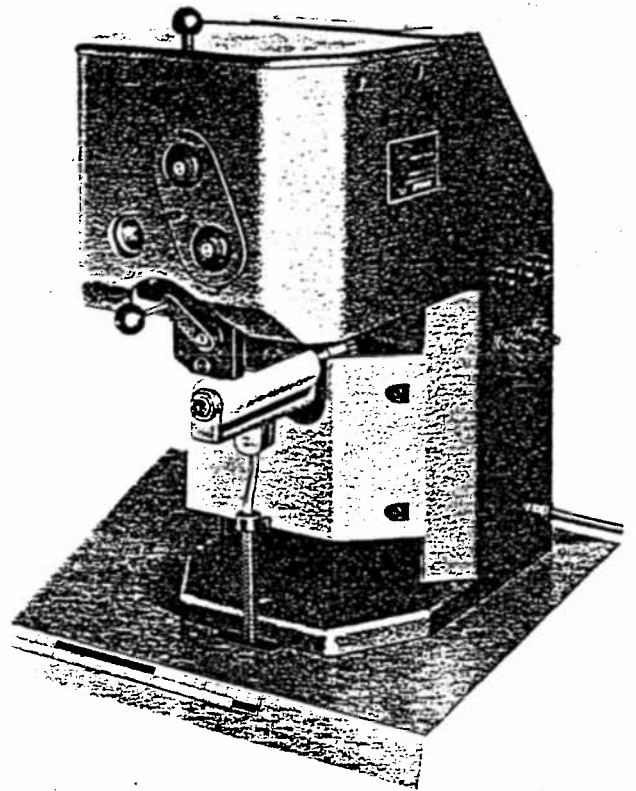
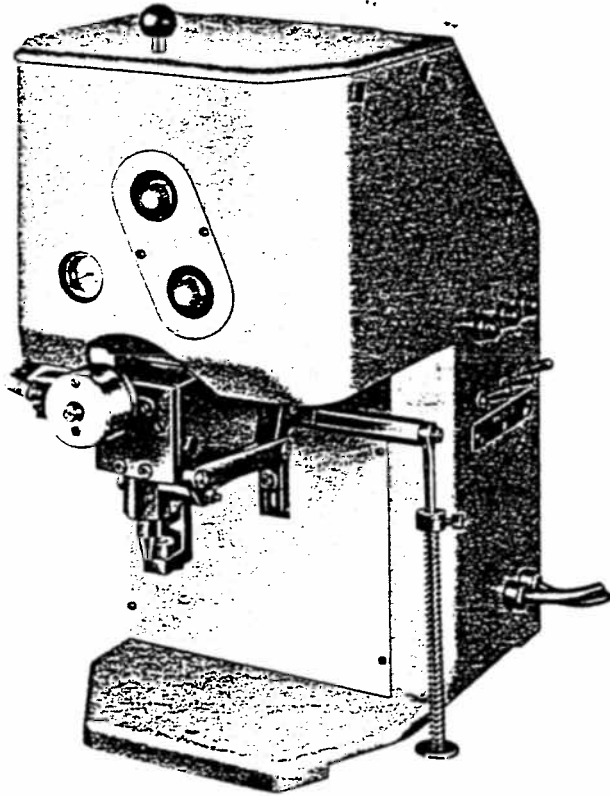
The effective component is the dry residue.

2.2 Application of solid adhesive

The development of those adhesives has permitted to build up machines combining the operation proper, folding or lasting for example, together with the application of the adhesive.

Also, from the manufacturing view point, one specific advantage is that the bonding can take place immediately after adhesive application or at a later stage after reactivation and, generally the adhesive is applied on one component only. As a result, a part from the folding and lasting machines which are relatively sophisticated there are a lot of dispensers and machines specially designed for hot melt adhesives which can be very practical for footwear manufacture.

The selection of adhesive has to be done in relation with the machine being utilized.



HOT MELT CEMENTING MACHINES

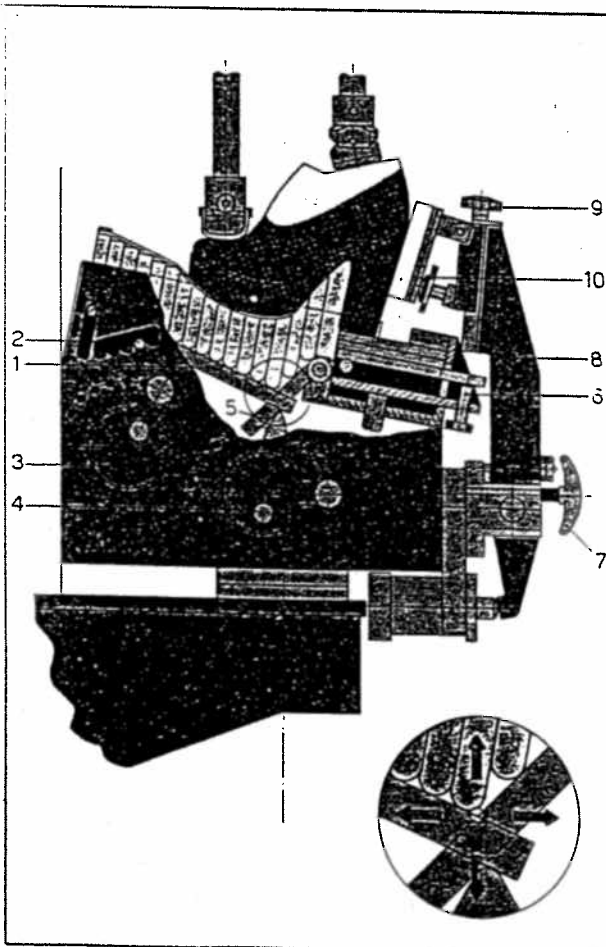
3. Re-activation

The dried film of adhesive on both upper and sole must be heat activated. This is done by infra-red radiation or by quartz halogen lamps. To check the activation temperature the use of chromatic pencils or chromatic powders is recommended.

4. Pressing

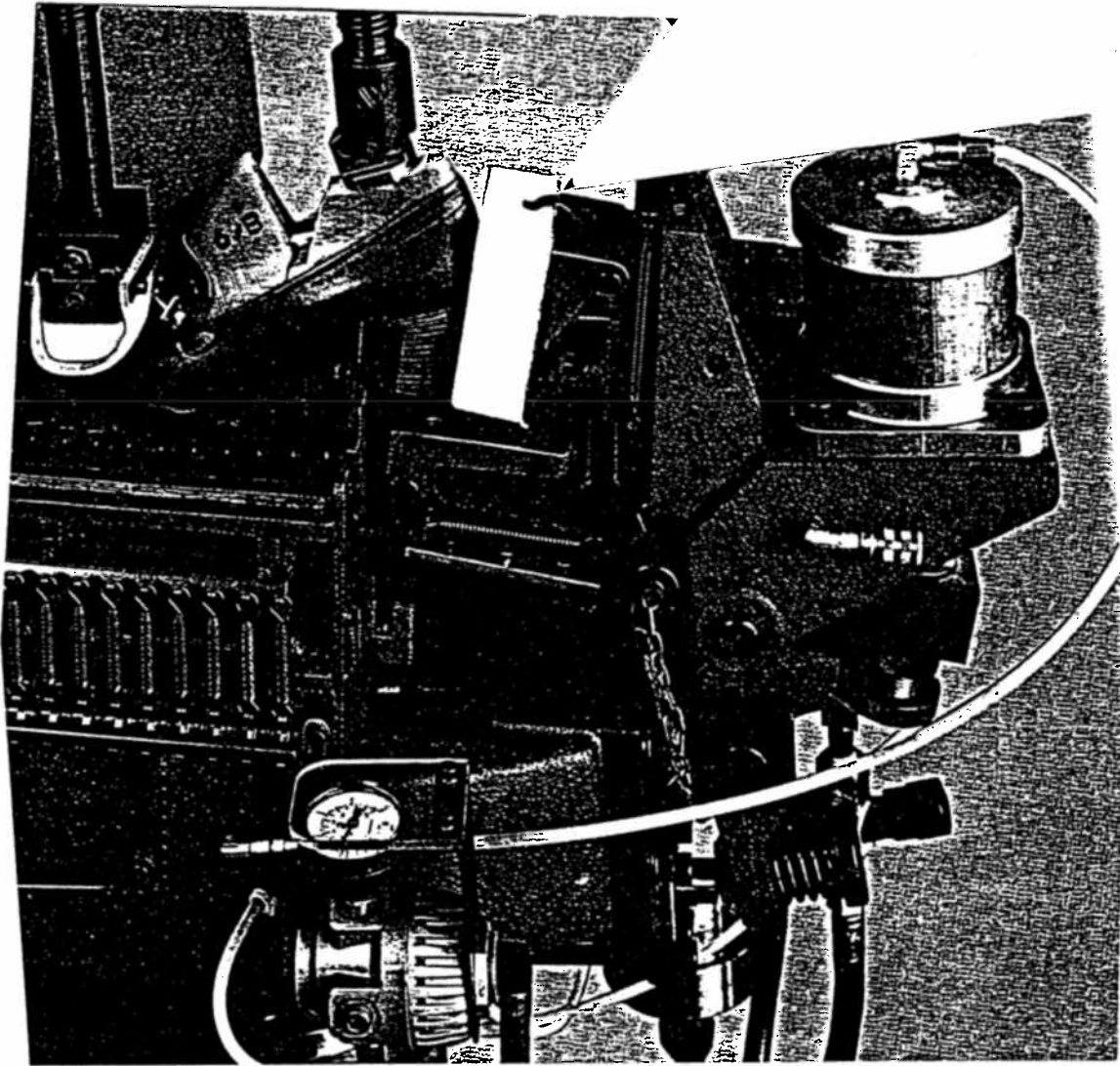
Pneumatic or hydraulic pressure may be employed. With pneumatic, the pressure should not exceed 4-5 bars or kg/cm².

With very compressible and soft materials the pressure should not deform the material to avoid strains when the pressure is released. The elasticity forces occurring when the material is coming back at its original shape are very high can destroy the bond.



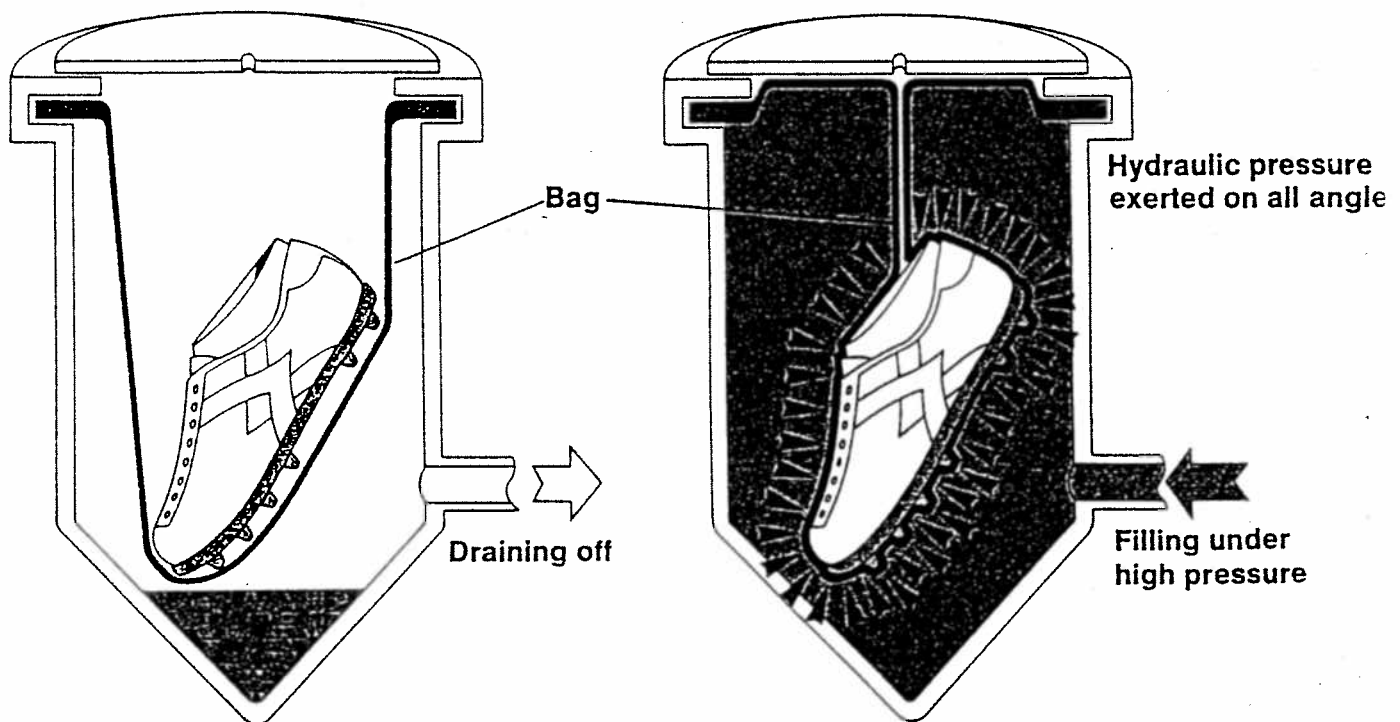
Adjustable hydraulic press, the cushion is replaced by lamellae in rubber. At low pressure, the lamellae come in close contact with the profile of the sole, high pressure is given afterwards.

Note the independent pressure to protect the heel.



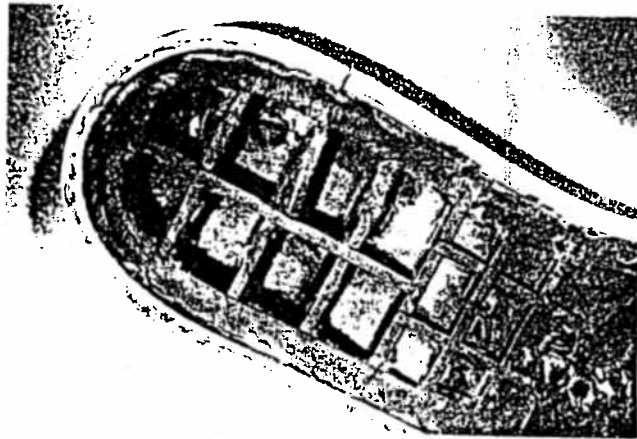
OPERATING

HYDRAULIC SOLE ATTACHING PRESS



G. SOME ADHESIVE FAILURES

1. The adhesive type is not compatible with one or both adherents
2. One or both adherents are not compatible with the adhesive.
3. Bad or insufficient surface preparation of the adherents.
4. The adhesive layer is insufficient, uneven, or in excess.
5. The adhesive layer was not dry when the adherents were bond together.
6. Insufficient re-activation or over re-activation.
7. Uneven pressing, to low or overpressing.



Breaking of the inner walls of a unit sole due to overpressing

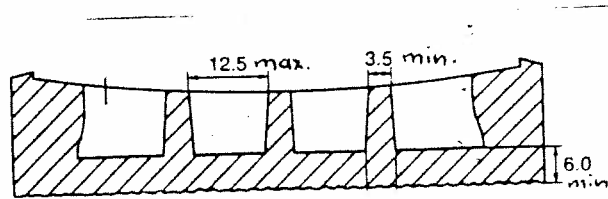
8. One or both adherents are weaker than the adhesive bond.
9. Migration of fat or plasticizers in the adhesive bond.
10. Low heat resistance of the adhesive bond.
11. Profile of unit soles, margin too narrow, cavities in the profile of the edges of heels, raised welt, etc.



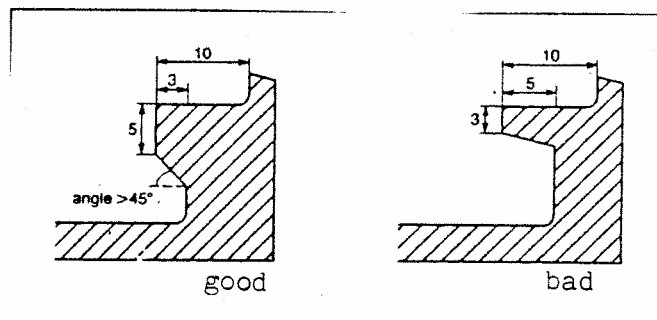
lasting margin to narrow



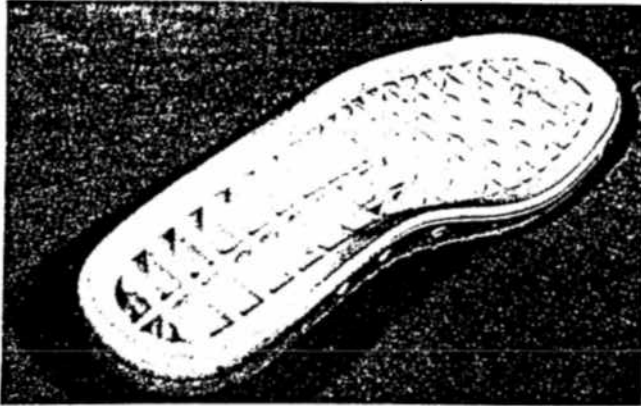
uneven width of lasting margin



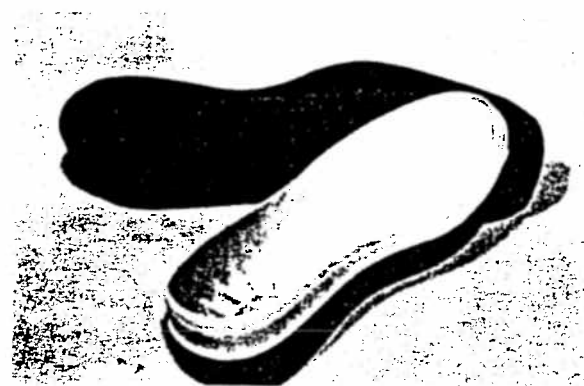
recommended profile



cavities in the edge of the heel

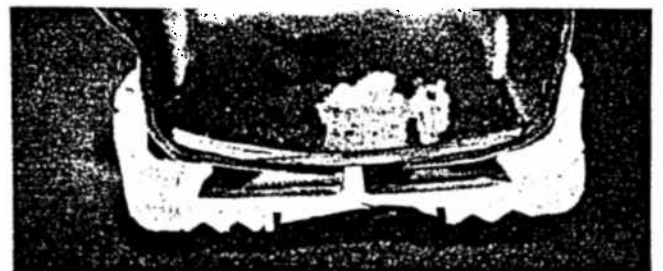


high
Slope on the lasting margin
will push the last forward



to high raised welt at the
back part

12. Insole to big or to narrow



13. Overthickness of the shank



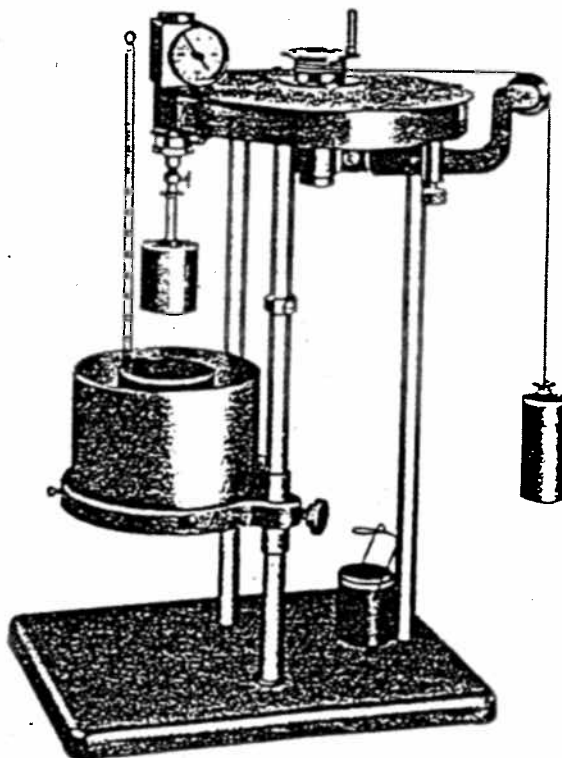
H. ADHESIVE AND ADHESIVE BOND TESTING

1. Viscosity

Viscosity (consistency) is the measure of fluid friction. The force of friction can be thought of as the energy required to move an object that rubs on another.

Viscosity may be considered as the internal friction resulting when a layer of fluid is made to move in relation to another layer.

A highly viscous adhesive is one which possesses a great deal of internal friction and will not pour or spread as easily as an adhesive of lesser viscosity.



Viscosimeter

A material's flow properties are important "product dimensions" - a complete description^{which} includes consideration of its pourability, penetrating characteristic, performance in a dipping or coating operation and the ease with which it may be handled or used (spreadability).

To test viscosity, a Brookfield viscometer, which is flexible and adaptable to a wide variety of measurements is used. This viscometer measures the force required to rotate a spindle in a fluid. The force to which it responds are extremely small and disturb the sensitivity of the measurement.

2. Solid Contents

Solid Contents or % Solids is the percentage by weight of the non-volatile matter in an adhesive.

For footwear and leathergoods adhesives, the oven method of testing the solids content is used. This is done by placing a weighed amount of adhesive in an oven (conditioned at 70°C) until all the volatile matter has evaporated or until getting a constant weight.

The solids is then calculated as follows:

$$\% \text{ solids} = \frac{(\text{wt. of container} + \text{dried sample}) - (\text{wt. of container})}{(\text{wt. of container} + \text{original sample}) - (\text{wt. of container})} \times 100$$

A Shoe manufacturer should consider the solids content in choosing an adhesive because this affects the bonding strength and the number of coats to be applied in a particular material.

For example, in the case of porous materials, several applications on one surface are required if the adhesive has low % solids.

3. Bond Strength

Bond Strength. To determine the bonding properties of adhesives, the peel test is performed by using the Tensile Strength Apparatus.

This test involves the stripping of a flexible member of an assembly that has been bonded with an adhesive to another member that may be flexible or rigid. For example, rubber to rubber, rubber to PVC, or PVC to PVC may be tested in peel.

The test consists of pulling the flexible member at an angle of 180° to induce peeling.

The stresses distribution in a peel test are complex and the force required to initiate and maintain stripping is influenced by the width of the specimen, the mechanical properties of the adherends and the strength of the adhesive.

Peel strength is defined as force per unit width necessary to separate the bonded parts of the substrates.

In testing, not only is the adhesive material evaluated but also the bonding technique which includes preparation of the surface, application, room condition (temperature and humidity at the time of application of adhesive) and the curing of the adhesive.

The accuracy and reproducibility of test results will depend on the conditions under which the bonding process is performed.

Before starting any evaluation, the individual conducting the test should have complete information on each of the following variables.

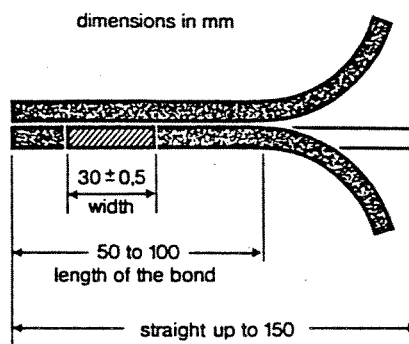
- (1) Procedure for preparing the surfaces prior to application of the adhesive, including the moisture content of the substrate and special surface treatments.
- (2) Complete mixing directions for the adhesive.
- (3) Conditions for the application of the adhesive including the thickness of film, no. of coats to be applied, whether to be applied to one or both surfaces and the conditions of drying.
- (4) Assembly conditions before application of pressure, including the room temperature, percentage relative humidity and whether there should be any open or closed assembly time.
- (5) Curing conditions, including the amount of pressure to be applied, the length of time under pressure and the temperature of the assembly when under pressure.
- (6) Conditioning procedure before testing, unless a standard procedure is specified, including the length of time, temperature and relative humidity.

4. Peel Strength Testing Procedure

4.1 Form of Substrate

2 strips of substrates or materials up to 15 cm. long and 3 cm. wide area are bonded to cover each other to a length of at least 5 cm. (see figure 1)

Figure 1



4.2 Surface Preparation of the Substrates

The surfaces of the substrates are cleaned or buffed depending on the adhesive to be used.

For PU adhesive, the bonding surfaces are freed from release agents, lacquers and finishes by cleaning the substrates with solvent and allowed to dry for 10 minutes.

For grafted adhesive, the surfaces are treated with primers and allowed to dry for 10 minutes.

4.3 Adhesive Conditioning

Adhesive to be used are conditioned at 29°C before use. For 2 component adhesives like Polyurethane, the Cross Linking Agent (hardener) is mixed with the adhesive & allowed to react for 10 minutes prior to application.

4.4 Adhesive Application

The adhesive is applied once or several times (depending on the porosity of the materials to be bonded) in the direction of the substrates.

If for example, the substrate is porous, several applications on one surface is required.

4.5 Drying

For grafted and contact cement, the adhesive is allowed to dry for 20 mins. before putting the two substrates together.

For Polyurethane, 2 testing methods are being done. First, the wet stick method wherein, the substrates are bonded after 3-7 minutes.

Second, the Heat reactivation method wherein, the substrates are stored at room temperature until the solvent has evaporated and within activation life. The substrates are then, placed in an activating apparatus for 5 minutes before bonding. (Activating apparatus usually involves an Infrared bulb or an oven set at a temperature of 70°C).

4.6) Pressing

A 10 kg. pressure is distributed evenly over the whole surface of the bonded material.

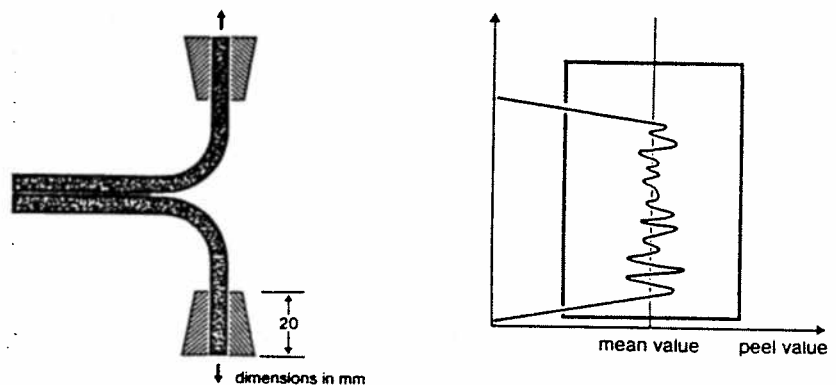
4.7 Curing

For standard testing, the bonded materials are stored for 3 days before carrying out the peel test. However, for quality control purposes in the adhesive industry, 24 hours curing is sufficient.

4.8 Measurement of the Peel Resistance

The uncoated ends of the substrates are bent over to either side and clamped in a tensile testing machine (see figure 2)

Figure 2



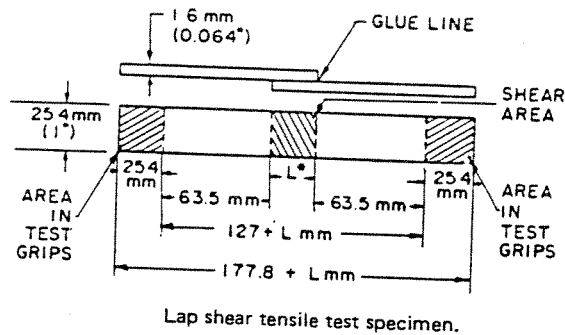
During the test the temperature of the substrates should be at 29°C. The ends are pulled apart at a speed of 100 mm/min.

For a pendulum or schopper type of tensile strength apparatus, the peeling force can be directly read and this is recorded as kg./cm.

However, for a digital type of tensile testing machine, the peeling force is determined by getting the mean value of a curve graphed by a recorder multiplied by a factor depending upon the sensitivity of the machine used.

5. Shear Test

In the shear test, two samples of adherents are bonded on each other (fig.) and the force of lateral separation is measured.



6. Creep Test

Heat resistance of a sole attaching adhesive is important if the shoes are exposed to high temperatures in wear.

The heat resistance is assessed by means of the CREEP test. Composite test pieces (adherent, adhesive, adherent) are clamped in an oven and loaded with 0.5 - 1.0 - 1.5 - 2.0 and 2.5 kg. weights. The temperature of the oven is raised to 60°C and held constant for 10 minutes.

The mass pieces are then removed, the test specimens released and distance peeled apart - the creep of the sample - is measured. If a sample creeps more than 30mm it is designated as "failed". The creep resistance is quoted as the highest mass at which failure does not occur.

7. Recommended Guidelines

7.1 Peel Test (method EEC/Feica A 3)

- initial resistance, 2 minutes after pressing
at least 1 newton/mm width
- after 5 days at 23°C and 50 % RH
at least 5 N/mm width
- after 7 days at 50°C and 2 days re-conditioning
at 23°C and 50 % RH
at least 80 % of the value after 5 days and not
less than 5 N/mm width

7.2 Creep Test (method EEC/Feica A 4)

under a load of 1.5 kg at 50°C
debonding less than 10 mm

8. Testing of adhesive during footwear manufacture

Adhesion problems are still the main concerns of footwear producers and adhesion failures are the main sources of complaints, accidents and rejects.

Adhesives are used in many operations of shoe making but it is oftentimes in the bonding sole to upper operation where a strong and permanent adhesion is required that difficulties occur.

There are two kinds of accidents that can happen due to the errors occurred at the junction between sole and upper : The sporadic ones where a unit shoe is damaged and those resulting in rejecting volumes of shoes or even of all the production.

The first ones are inherent to a manufacturing or assembling process, their percentage must be kept as low as possible by careful control of the successive operations in the preparation of the materials, the application of the adhesive and in the bonding techniques.

One must keep in mind that the repetition of an operation by a worker implies a kind of heterogeneity in the resulting work and that all the pieces produced during a working day will not be exactly the same.

Hence, there is a necessity of quality control at each step of the production. That control will be made and as a result, some shoes or components will have to be repaired or reworked. A minimum level of rejects should be fixed. If that level is exceeded something is wrong in the equipment or in the material or in the handling.

On the other hand, there can be problems in a serie of shoes, on a part or on all the production. The failure becomes systematic.

If this is discovered during or at the end of the production, the origin of the trouble can be determined and the consequences of the failure can be corrected.

If it occurs after shipping or when the shoes are at the retail shop it becomes a disaster.

In such accidents, it should be too easy to incriminate the adhesive. Usually, the origin of the failure will be in the soling material and in its preparation.

All the man made soling materials are compounds of different chemicals. Natural or synthetic rubbers and other elastomeres are blended with other substances such as metallic oxides, antioxidants, pigments, plasticizers and fats. Sometimes, different types of elastomeres are mixed together.

Those blendings are intended to modify or to improve the physical properties of the finished product : elasticity, hardness, density, abrasion and flexing endurance. It is also intended to adapt the price, usually to reduce the cost of the soling material.

In vulcanizing or injection techniques, moulds and other metal parts of the machines are protected with silicones or fluoride chemicals to avoid adherence with the rubber-like materials.

Consequence of blending is the presence of substances that can migrate to the outer parts of the sole where they oxidise or form soaps with the metallic oxides giving a white fatty "bloom" which offer resistance to the action of the adhesive. If rubbers contain too much fats or PVC contains too much plasticizers, migration can occur in the adhesive film on the finished shoe.

In the same way the mould lubricants can oppose themselves to the adhesive.

On the other hand, most of the elastomeres can be expanded, the action of the blowing agent, depending namely of the temperature, is very variable and holes of different sizes are blown reducing the structural cohesion of the material. In this case, the rupture of the bond sole/upper will come in the material itself and not in the adhesive.

There are materials that are difficult to bond, so that generally all man-made soling materials have to be carefully tested, whether they are newly developed materials or the traditional ones. For each delivery and certainly each time that a long stored material is used, it should be checked.

This can easily and quickly be done in the factory on small strips of sole and upper materials, e.g. strips of 3 x 15 cm.

After a standard or different types of preparation, adhesive is applied, dried and reactivated. Just before bonding, a folded paper is inserted at both ends of the sample piece. Five minutes after pressing, the initial resistance is tested by hand. With a little bit of practice, the bond can easily be evaluated for its :

1. Adhesion failure or detachment of the adhesive film from one of the materials, (fig. 5a and 5b), index A.
2. Cohesive failure or separation within the adhesive film without detachment from the material, (fig. 6), index C.
3. Non-coalescence or failure of the two adhesive film to combine without detachment from the material (fig. 7), index N.
4. Breakdown of a material of low structural strength at its surface, (fig. 8a and 8b), index S.
5. Partial or complete breakdown of material, (fig. 9a and 9b), index M.

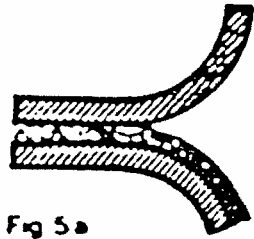


Fig 5a

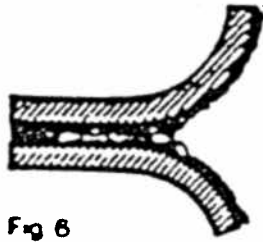


Fig 6

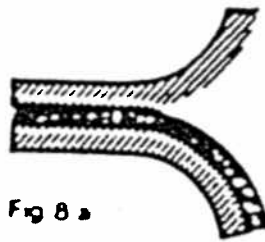


Fig 8a

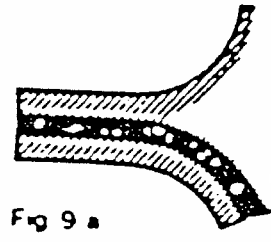


Fig 9a

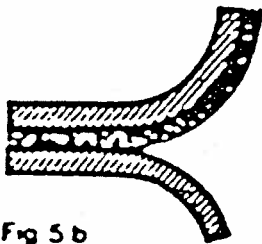


Fig 5b

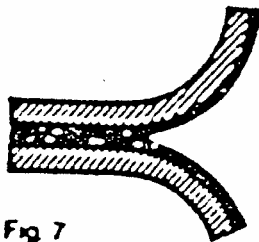


Fig 7



Fig 8b

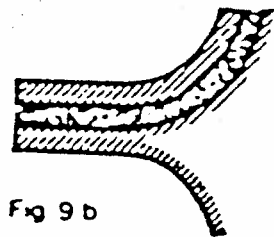


Fig 9b

- | | |
|----------------|------------------------------------|
| fig. 5 a + 5 b | Adhesion failure |
| fig. 6 | Cohesive failure |
| fig. 7 | Non-coalescence |
| fig. 8 a + 8 b | Breakdown of a material at surface |
| fig. 9 a + 9 b | partial or complete breakdown |

If adhesion failure is observed, there is incompatibility between materials and adhesive, and other type of preparation should be investigated or another adhesive should be tested. Usually, there will be no improvement of the bond by ageing.

If there is cohesive failure or non-coalescence, the adhesive film itself is not strong enough, or the two adhesive are not compatible, or the film was not dry.

Breakdown in the materials is self explanatory indeed, the materials are weaker than the adhesive.

Two or three days after testing the initial strength, the testing is repeated at the other end of the sample piece and the evaluation is done in the same way.

Such kind of testing and evaluation may be considered as of poor accuracy and will depend from the operator. Only evident failures will be observed but as safety measure in the factory, this is already good enough. For more accurate testing, a tensile machine should be used.

Another possibility of testing sole adhesion in the factory is to insert a piece of folded strong paper at the top or at the heel of the shoe just before pressing. Before delasting, the adherence of the sole is tested on a part or on all the bottom surface of the shoe. As the sole is partially separated from the upper through the piece of paper and as the upper is still on the last, the shoe is not damaged and can be easily repaired.

For more accurate testing, an apparatus like the Satra adhesion tester is used or a special device is fixed on the lower jaw of the testing machine in such a way that the shoe can be placed on it. A metal wire passing through two holes made in the edge of the sole is fixed in the upper clamp and the sole is separated from the shoe.

Taking into account, the high rate of production in factories making sportshoes, control and testing of sole adhesion is there of uttermost importance.

As those footwear have generally injected soles, testing on sample pieces is impossible, except if the injection machine is equipped with a special mould for test pieces.

Testing of sole detachment is also more difficult than on conventional shoes, mainly because of the shape of the sole with raised top and edges.

There is a possibility to fix a piece of heat resistant material at the top or at the heel of the lasted shoe just before injection, or to cover the top with a kind of sock in such a way that part of the sole can be gripped for the test.

In some factories, the shoe to be tested is cut along the median line going from top to heel and the separation is made going from the center of the sole to the edges.

Conclusion

Considering the construction of a shoe, the footwear making technology and the wear conditions of shoes, one must admit that the bonding of upper to sole is a weak part of the assembly and that accidents or failures are always possible.

Hence, there is a need for a strict control

Cost of control and testing will soon or later be compensated by the decrease of repairs and rejects.

ANNEX I

HEALTH PROTECTION AND SAFETY MEASURES :

Latex

Little danger is associated with the handling of natural latex even when it is in ammoniac suspension.

Ammonia gas causes irritation of the respiratory tract at concentrations above 100 mg/m^3 . The maximum concentration per hour is between 210 and 350 mg/m^3 . Such high concentrations are only existing in chemical plants.

Solvent Adhesives

The use of benzene has been discontinued in some countries because of its highly toxic properties.

Most of the solvents are flammable and harmful to health.

Flammable liquids should be handled in containers designed to minimize the occurrence of spillage. They should not be used where there are fire hazards. Smoking should be prohibited in the rooms in which they are used.

The use of the most dangerous solvents like benzene, toluène, xylene and the more dangerous chlorinated hydrocarbons should be discontinued and substitutes such as petroleum solvents and tetrachloroethylene are used.

In many processes significant quantities of solvent may evolve. These processes should be conducted in closed plant, or within an enclosure or under a hood to which exhaust ventilation is applied to remove the fumes before they enter the air of the workroom.

Many of the processes in which adhesives are applied proceed at elevated temperatures and are therefore associated with a high evolution of vapours.

Most of the solvents used are capable of dissolving the natural oils of the skin and causing dermatitis on the hands of the operators.

Polyurethane Adhesives and Two Component Systems

Exposure to the vapors of di-isocyanates can cause severe pulmonary effects ... The maximum value has been laid down at 0.01 ppm or 1 mg/m³ of air.

Different individuals differ in their sensitivity to di-isocyanates. Allergic persons especially asthmatic and persons with a tendency to bronchial ailment or other disorders of the respiratory system should be excluded from work with isocyanates as a matter of principle.

The work places must be thoroughly ventilated especially the places where the adhesive films are activated by heat because of higher formation of vapours.

Danger of Benzene

Benzene, toluene and xylene have acute narcotic action. Vapors of those solvents injure blood forming tissues even at low concentrations. Their action is insidious and ultimate injury is incurable.

The early symptoms are: fatigue, loss of appetite, headaches, dizziness, anaemic appearance.

For some considerable time, the patient's general condition remains good although there is pallor, hypotension and increase in temperature.

Blood examination at this stage may reveal only slight abnormality. Later, however, a more significant change in the blood picture appears (leukemia) and destruction of the elements of the bone marrow may develop.

Metabolism

The fate of benzene in the body has been the subject of considerable study. A large proportion is eliminated in the exhaled air but 15-60% depending on the circumstances is metabolised. The main metabolic transformation is oxydation with the production of phenols. This oxidation phase is centered mainly on the liver and is followed by an elimination of alkaline salts in the urine (urines light to dark brown on exposure to air).

Health Precautions

Whenever possible adhesives and other substances without benzene and with a low organic solvent should be used.

When benzene is used as a solvent, all the precautions to prevent the escape of vapors into the workroom atmosphere must be taken with meticulous thoroughness: good ventilation of working area and workroom, testing of the workroom atmosphere to ensure that the ventilation is effective, labelling of the containers with skull and cross bones symbol, labeling of the designation of the product together with its benzene content by volume and medical supervision.

* metabolism: the process in the building up and destruction of living cells,
chemical reactions in living cells

S O L V E N T	DENSITY of VAPORS	M.A.C. in p.p.m.	0.1 RFD 50% in p.p.m.
TOLUENE	3.14	100	337
METHYLETHYLKETONE	2.5	200	1,074
ACETONE	2	1,000	2,348
ETHYL ACETATE	3.04	400	58

M.A.C. Maximum admisible concentration
R.F.D Respiratory Frequency Diminution
p.p.m. W/V 10^6

Ventilation of Working Places

As most of the solvents give vapor with a density higher as that of the air, all ventilation systems should have air entry at the ceiling and air exhaust at the floor (Fig. 1). The exhauster should be at least 8 meter from the air blower to avoid recycling of the air. The exhauster should not be close to other working places or neighbor houses.

Ventilated Tables

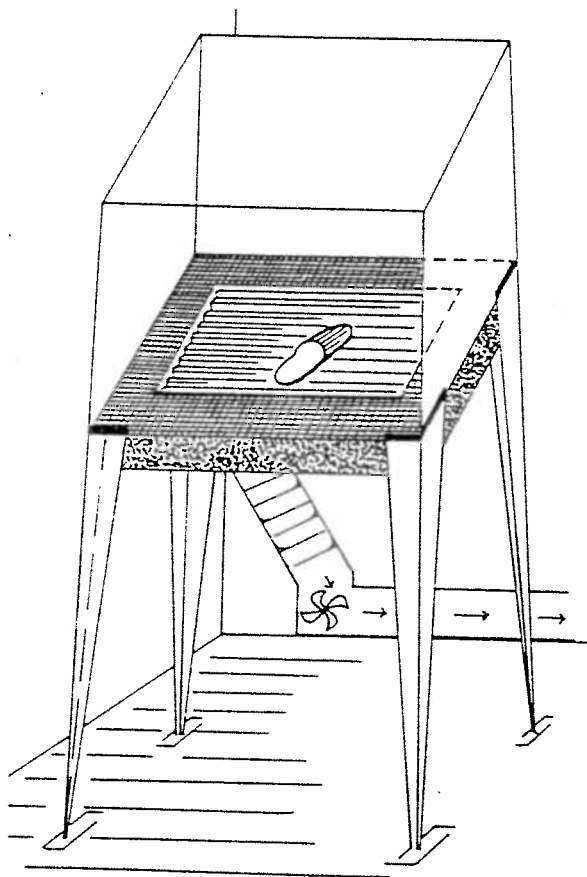
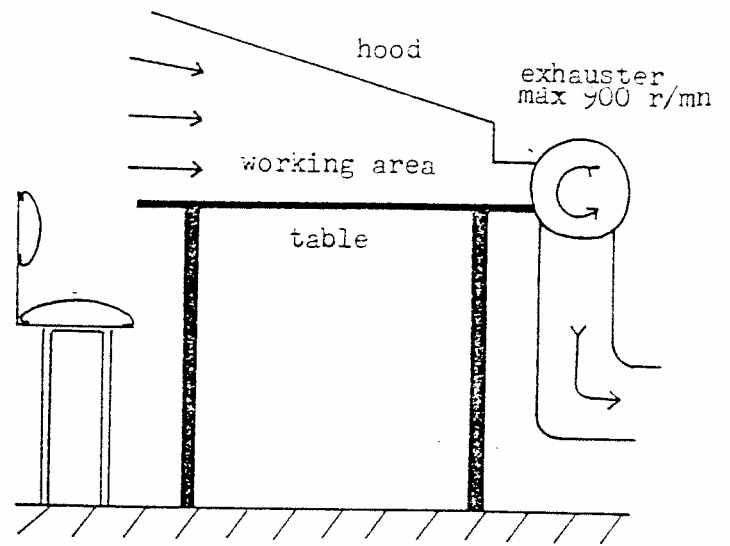
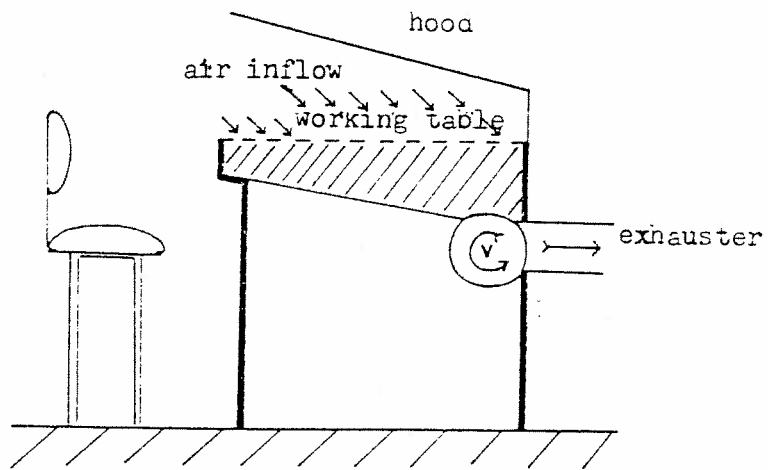
Figures 2 - 3 and 4 show some types of ventilated tables for footwear industry.

The recommended working area is 0.60 m X 0.80 m and is made of a screen or netting.

The exhauster is at the bottom or at the back of the table. Exhauster at the back gives risk of clogging.

To be effective, the table must be covered with a hood. The speed of the exhauster should not be higher than 900 revolutions per minute to avoid moise.

The speed of the air flow should be between 0.30 and 0.40 m/sec. Above 0.40 m/sec., solvents evaporate too fast, below 0.30 m/sec., the air flow is inefficient.



Limits for Occupational Exposure

Substance	France		USA	USSR	W. Germany (40 h/week)	United Kingdom		Notes
	Maximum value	Average value (8 h)				8 h TWA	10 min TWA	
Ethyl acetate	—	1400	1400	200	1400	1400	—	
Acetone	—	1800	1780	200	2400	2400	3000	
Acetic acid	25	—	25	5	25	25	37	
Hydrochloric acid	7.5	—	7	5	7	7	7	
Hydrocyanic acid	10	2	10	0.3	11	10	10	
Formic acid	9	—	9	1	9	9	—	
Nitric acid	10	5	5	—	25	5	10	
Sulphuric acid	3	1	1	1	1	1	—	
Butyl alcohol	150	—	150	10	300	150	150	n-Butyl alcohol
Ethyl alcohol	—	1900	1900	1000	1900	1900	—	
Methyl alcohol	1300	260	260	5	260	260	310	
Formaldehyde	3	—	1.5	0.5	1.2	2.5	2.5	
Ammonia	36	18	18	20	35	18	27	
Aniline	—	10	10	0.1	8	10	20	
Benzene	—	15	30	15/5	26	30	—	
Butyl oxitol	—	120	120	—	100	240	720	For synonyms, see below (1)
Calcium carbonate	—	—	10	—	—	—	—	
Calcium hydroxide	—	—	5	—	—	5	—	
Monochlorobenzene	—	—	350	50	230	350	—	
Sodium chloride	—	—	—	5	—	—	—	
Chromium III compounds (as Cr)	—	—	0.5	—	—	0.5	—	
Chromium VI compounds (as Cr)	—	—	0.05	—	—	0.05	—	
Dimethylamine	18	—	18	1	18	18	—	
Oxitol	—	—	19	5	75	370	560	For synonyms, see below (2)
Ethyl mercaptan	—	1	1	1	1	1	3	
Hexane	—	170	180	—	180	360	450	n-Hexane
Hydrogen sulphide	14	7	14	10	15	14	21	
Kerosine	—	—	—	—	300	—	—	
Magnesium oxide	—	—	10	—	6 (a)	10 (b)	—	(a) Dust, (b) fume (as Mg)
Manganese (dust)	—	—	5	—	5	5	5	
Methyl butyl ketone (MBK)	35	20	20	—	21	100	165	
Methyl ethyl ketone (MEK)	—	600	590	200	590	590	885	
Methyl isobutyl ketone (MIBK)	—	205	205	5	400	410	510	
Methyl mercaptan	—	1	1	0.8	1	1	—	
Carbon monoxide	—	55	55	20	33	55	440	
Ozone	0.4	0.2	0.2	0.1	0.2	0.2	0.6	
Pentachlorophenol	—	—	0.5	0.1	0.5	0.5	1.5	
Hydrogen peroxide	—	—	1.5	—	1.4	1.5	3.0	
Phenol	—	19	19	0.3	19	19	38	
Pyrocatechol	—	—	20	—	—	20	—	
Sodium carbonate	—	—	—	2	—	—	—	
Sodium hydroxide	—	2	2	—	—	—	—	
Sulphur dioxide	10	5	5	10	5	5	13	
Toluene	550	375	375	50	750	375	560	
Trichloroethylene	1080	405	270	10	260	535	802	
White spirit	—	—	525	—	—	575	720	
Perchloroethylene	—	—	—	—	345	670	1000	For synonyms, see below (3)

Notes: (a) mg/m³ used throughout, not the more usual ppm.

(1) also known as 2 butoxyethanol, butyl glycol, butyl cellosolve, etc.

(2) Also known as 2 ethoxyethanol, ethyl glycol, cellosolve, ethyl cellosolve, etc.

(3) Also known as "Perk": tetrachloroethylene, tetrachloroethene, etc.

To convert mg/m³ to ppm: Determine F=mol.wt./24.1; Then ppm=mg/m³/F.

ANNEX II

STANDARD DEFINITIONS OF SOME TERMS RELATING TO ADHESIVES

ASTM Designation D-907-74

- | | |
|-----------------------------|---|
| ADHEREND | - a body which is held to another body by an adhesive. |
| ADHESION | - the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action, or both. |
| ADHESIVE | - a substance capable of holding materials together by surface attachment |
| ADHESIVE, solvent activated | - a dry adhesive film that is rendered tacky just prior to use by application of a solvent. |
| ADHESIVE, warm-setting | - a term that is sometimes used as a synonym for Intermediate Temperature Setting Adhesive |
| ADHESIVE DISPERSION | - a two-phase system in which one phase is suspended in a liquid. |
| ASSEMBLY | - a group of materials or parts, including adhesive, which has been placed together for bonding or which has been bonded together. |
| BOND, n | - the union of materials by adhesives |
| BOND, v | - to unite materials by means of an adhesive |
| BOND STRENGTH | - the unit load applied in tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly with failure occurring in or near the plane of the bond. |

CATALYST

- a substance that markedly speeds up the cure of an adhesive when added in minor quantity as compared to the amounts of the primary reactants.

COHESION

- the state in which the particles of a single substance are held together by primary or secondary valence forces. As used in the adhesive field, the state in which the particles of the adhesive (or the adherend) are held together.

CREEP

- the dimensional change with time of a material under load, following the initial instantaneous elastic or rapid deformation. Creep at room temperature is sometimes called Cold Flow.

CURE

- to change the physical properties of an adhesive by chemical reaction which may be condensation, polymerization, or vulcanization; usually accomplished by the action of heat and catalyst, alone or in combination, with or without pressure.

FILLER

- a relatively nonadhesive substance added to an adhesive to improve its working properties, permanence, strength, or other qualities.

FLOW

- movement of an adhesive during the bonding process, before the adhesive is set.

GLUE

- originally, a hard gelatin obtained from hides, tendons, cartilage, bones, etc. of animals. Also, an adhesive prepared from this substance by heating with water. Through general use the term is now synonymous with the term "adhesive".

HARDENER	- a substance or mixture of substances added to an adhesive to promote or control the curing reaction by taking part in it. The term is also used to designate a substance added to control the degree of hardness of the cured film.
JOINT	- the location at which two adherends are held together with a layer of adhesive.
LAMINATE , n	- a product made by bonding together two or more layers of material or materials.
LAMINATE, v	- to unite layers of material with adhesive.
PENETRATION	- the entering of an adhesive into an adherend.
PERMANENCE	- the resistance of an adhesive bond to deteriorating influences.
PLASTICITY	- a property of adhesives that allows the material to be deformed continuously and permanently without rupture upon the application of a force that exceeds the yield value of the material.
PLASTICIZER	- a material incorporated in an adhesive to increase its flexibility, workability, or distensibility. The addition of the plasticizer may cause a reduction in melt viscosity, lower the temperature of the second-order transition, or lower the elastic modulus of the solidified adhesive.
POT LIFE	- see working life
PRIMER	- a coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond.
RELEASE PAPER	- a sheet, serving as a protectant and/or carrier for an adhesive film or mass, which is easily removed from the film or mass prior to use.

- SET
- to convert an adhesive into a fixed or hardened state by chemical or physical action, such as condensation, polymerization, oxidation, vulcanization, gelation, hydration, or evaporation of volatile constituents.
- SOLID CONTENT
- the percentage by weight of the nonvolatile matter in an adhesive.
- SPREAD
- the quantity of adhesive per unit joint area applied to an adherend, usually expressed in points of adhesive per thousand square feet of joint area.
 - (1) single spread refers to application of adhesive to only one adherend of a joint.
 - (2) double spread refers to application of adhesive to both adherends of a joint.
- STORAGE LIFE
- the period of time during which a packaged adhesive can be stored under specified temperature conditions and remain suitable for use. Sometimes called shelf life.
- STRENGTH, DRY
- the strength of an adhesive joint determined immediately after drying under specified conditions or after a period of conditioning in the standard laboratory atmosphere.
- STRENGTH, WET
- the strength of an adhesive joint determined immediately after removal from a liquid in which it has been immersed under specified conditions of time, temperature, and pressure.
- STRINGINESS
- the property of an adhesive that results in the formation of filaments or threads when adhesive transfer surfaces are separated.

- SUBSTRATE
- a material upon the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than adherend.
- SURFACE PREPARATION
- a physical and/or chemical preparation of an adherend to render it suitable for adhesive joining.
- TACK
- the property of an adhesive that enables it to form a bond of measurable strength immediately after adhesive and adherend are brought into contact under low pressure.
- TEMPERATURE, curing
- the temperature to which an adhesive or an assembly is subjected to cure the adhesive.
- NOTE: The temperature attained by the adhesive on the process of curing it (adhesive curing temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly curing temperature)
- TEMPERATURE, drying
- the temperature to which an adhesive on an adherend or in an assembly or the assembly itself is subjected to dry the adhesive.
- NOTE: The temperature attained by the adhesive in the process of the atmosphere surrounding the assembly.
- TEMPERATURE, setting
- the temperature to which an adhesive or an assembly is subjected to set the adhesive.

NOTE: The temperature attained by the adhesive in the process of setting it (adhesive setting temperature) may differ from the temperature of the atmosphere surrounding the assembly

- THINNER
- a volatile liquid added to an adhesive to modify the consistency or other properties.
- THIXOTROPY
- a property of adhesive systems to thin upon isothermal agitation and to thicken upon subsequent rest.
- TIME ASSEMBLY
- the time interval between the spreading of the adhesive on the adherend and the application of pressure or heat, or both, to the assembly.
- TIME, curing
- the period of time during which an assembly is subjected to heat or pressure, or both, to cure the adhesive.
- TIME, drying
- the period of time during which an adhesive on an adherend or an assembly is allowed to dry with or without the application of heat or pressure, or both.
- TIME, joint conditioning
- the time interval between the removal of the joint from the conditions of heat or pressure, or both, used to accomplish bonding and the attainment of approximately maximum bond strength. Sometime called Joint Aging Time.
- TIME, setting
- the period of time during which an assembly is subjected to heat or pressure, or both, to set the adhesive.
- VISCOSITY
- the ratio of the shear stress existing between laminae of moving fluid and the rate of shear between these laminae.

VULCANIZATION

- a chemical reaction in which the physical properties of a rubber are changed in the direction of decreased plastic flow, less surface tackiness, and increased tensile strength by reacting it with sulfur or other suitable agents.

* * * * *

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