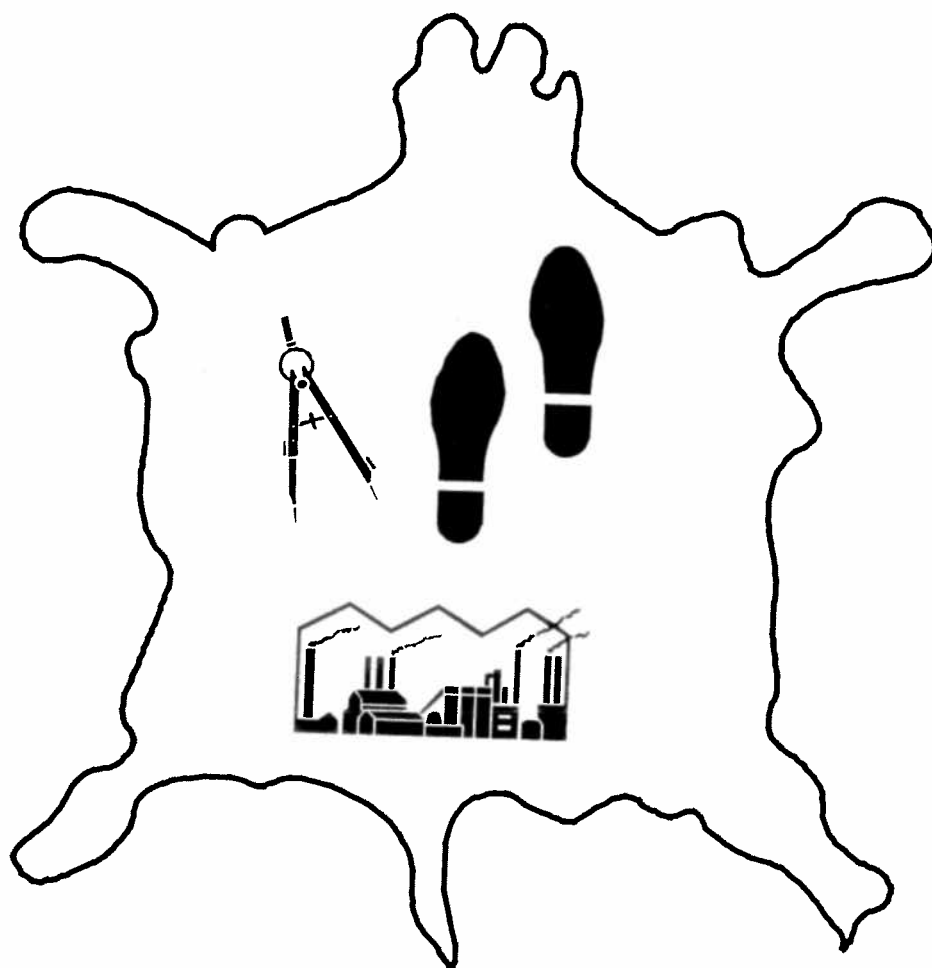


SHOE INDUSTRY CERTIFICATE COURSE



ELASTOMERS AND PLASTOMERS*



* This document has been produced without formal editing



This learning element was developed by the UNIDO Leather Unit's staff, its experts and the consultants of the Clothing and Footwear Institute (UK) for the project US/PHI/85/109 and is a part of a complete Footwear Industry Certificate course. The material is made available to other UNIDO projects and may be used by UNIDO experts as training aid and given, fully or partly, as hand-out for students and trainees.

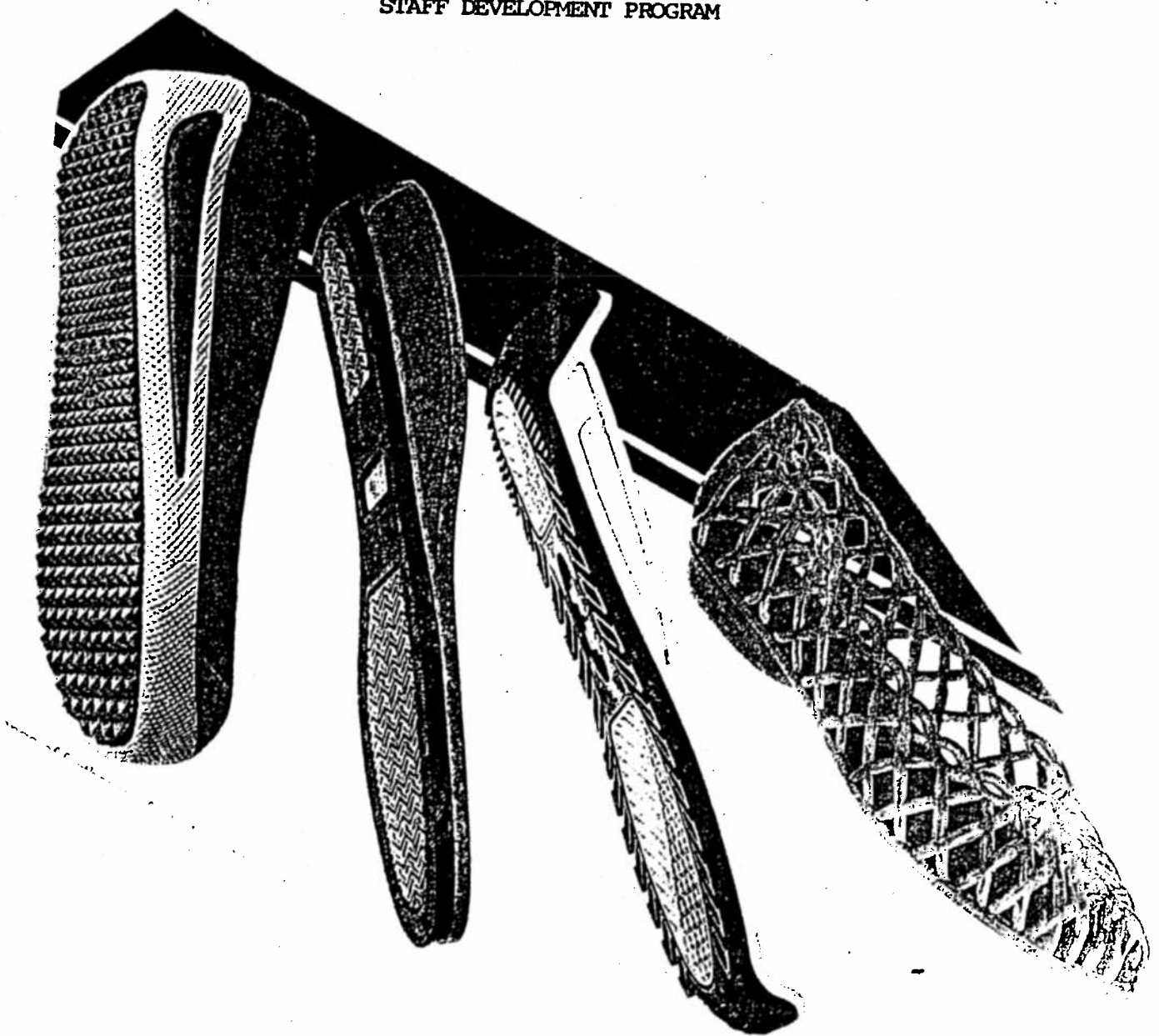
The complete Certificate Course includes the following learning elements:

Certificate course

- Feet and last
- Basic design
- Pattern cutting
- Upper clicking
- Closing
- Making
- Textiles and synthetic materials
- Elastomers and plastomers
- Purchasing and storing
- Quality determination and control
- Elements of physics
- General management
- Production management
- Industrial Law
- Industrial accountancy
- Electricity and applied mechanics
- Economics
- SI metric system of measurement
- Marketing
- Mathematics
- Elements of chemistry

FOOTWEAR AND LEATHERGOODS INDUSTRY CENTER

STAFF DEVELOPMENT PROGRAM



ELASTOMERS
AND
PLASTOMERS

FLIC/CFI 19.2

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ELASTOMERS AND PLASTOMERS

Elastomers and plastomers are natural or artificial materials produced by chemical or physical reactions.

They can be inorganic (mineral) or organic (carbon)

e.g. mica and glass are inorganic
rubber, PVC, etc. are organic

Plastomers are hard macromolecular materials. In given temperature ranges - specific for each of them - they are becoming plastic, soft and can be moulded. They can be fluidoplastics, thermoplastics or duroplastics.

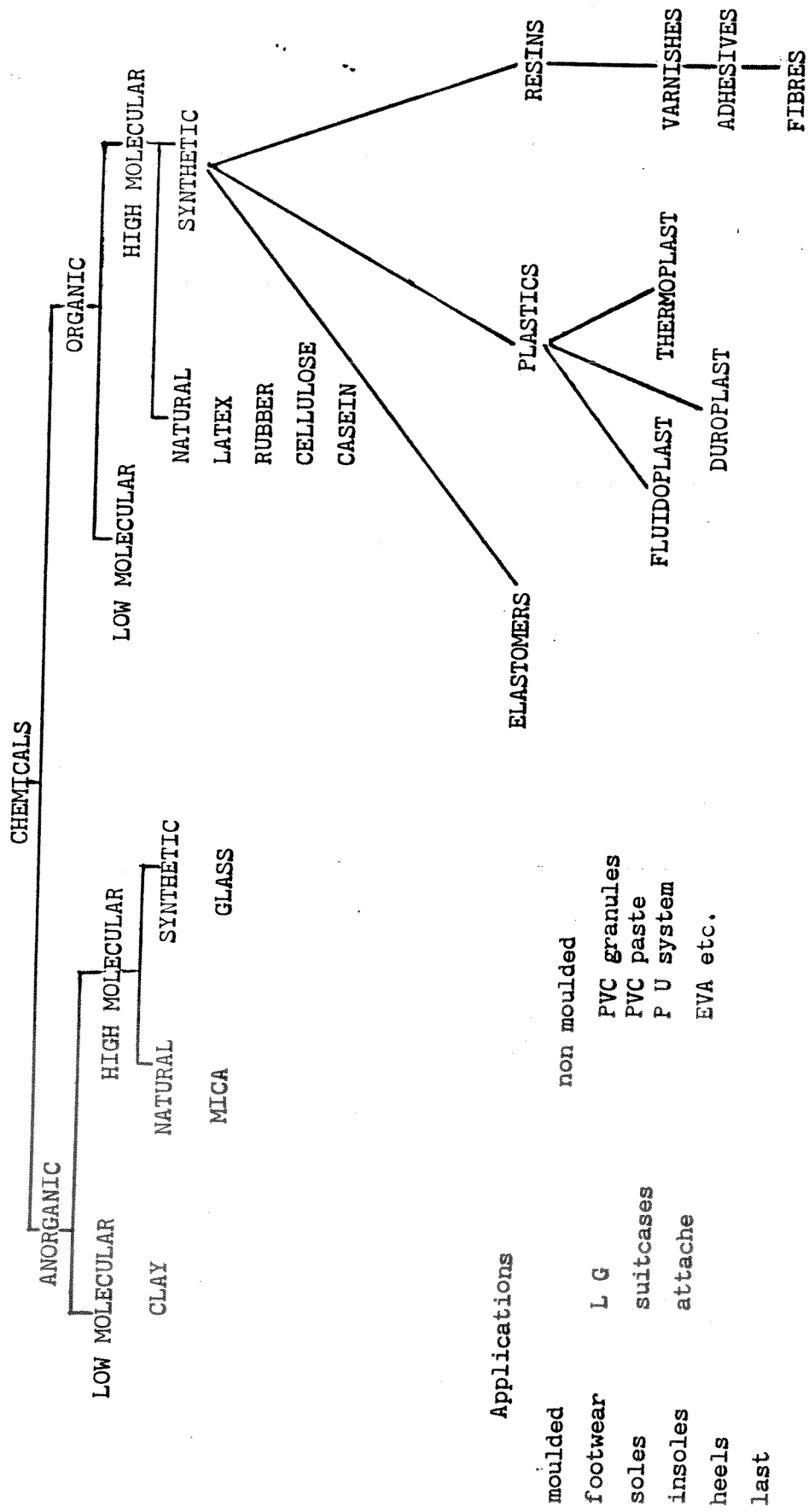
Elastomers are soft organic macromolecular materials, having a softening point in given temperature ranges and rubberlike properties (elasticity, resilience, etc.)

There are many utilizations of plastomers and elastomers in footwear and leathergoods manufacture :

plastomers : heels, shanks, last, suitcases, attache-cases, etc.
elastomers : soles, insoles, coated fabrics, adhesives, etc.

Compared to leather, the advantages of synthetic materials are :

- homogeneity of quality (good or bad)
- possibility to improve or modify the physico-chemical properties
- important availability of raw material
- possibility of producing big quantities
- cheaper prices
- more rational utilization in manufacture of goods.



A. The natural elastomers and plastomers

1. Rubber

Natural rubber is the most used material. It comes from a tree. Its origin is a south american tree, called by the Indian "Cahuchu", where other species like the "Hevea" originated.

The tree produces a liquid which is tapped from a cut in the bark and is known as latex.

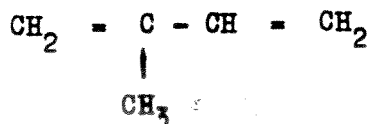
Latex is a liquid similar to milk. It is an emulsion of rubber in water. This means that very small particles of rubber are dispersed in the water serum of the plant.

Just like milk, the latex emulsion is only stable in given conditions and has a very short life time.

After coagulation with an acid, the precipitate is pressed and dried to give pale "crepe" or cured by smoking into smoked sheets.

These two materials are the raw materials for natural rubber goods.

Natural rubber is a complex chemical that can be defined as a natural polymer of isoprene C_5H_8



The molecular chains in natural rubber are very long, this makes it difficult to compound and mould directly.

Natural rubber must be treated by mastification, which depolymerizes the chain molecules, reducing the molecular weight.

It is performed on a mixing mill having two rolls running at slightly different speeds in opposite directions and with a narrow gap between them. The heavy shear forces exerted on the materials in these machines cause the long chain molecules to tear. There is also an increase in temperature due to the kneading action.

After the material has been put through the mill two or three times a rough sheet is obtained. It is only at this stage that the full mastification effect can be obtained. The sheet is passed between the rolls again and again. To prevent the sheet from continuing to circulate, the front part must be taken off the roll with a knife. Thereafter, the material is returned to the mill until the required degree of depolymerization has been reached. The material is then soft enough for incorporation of fillers and other additives.

The additives are usually :

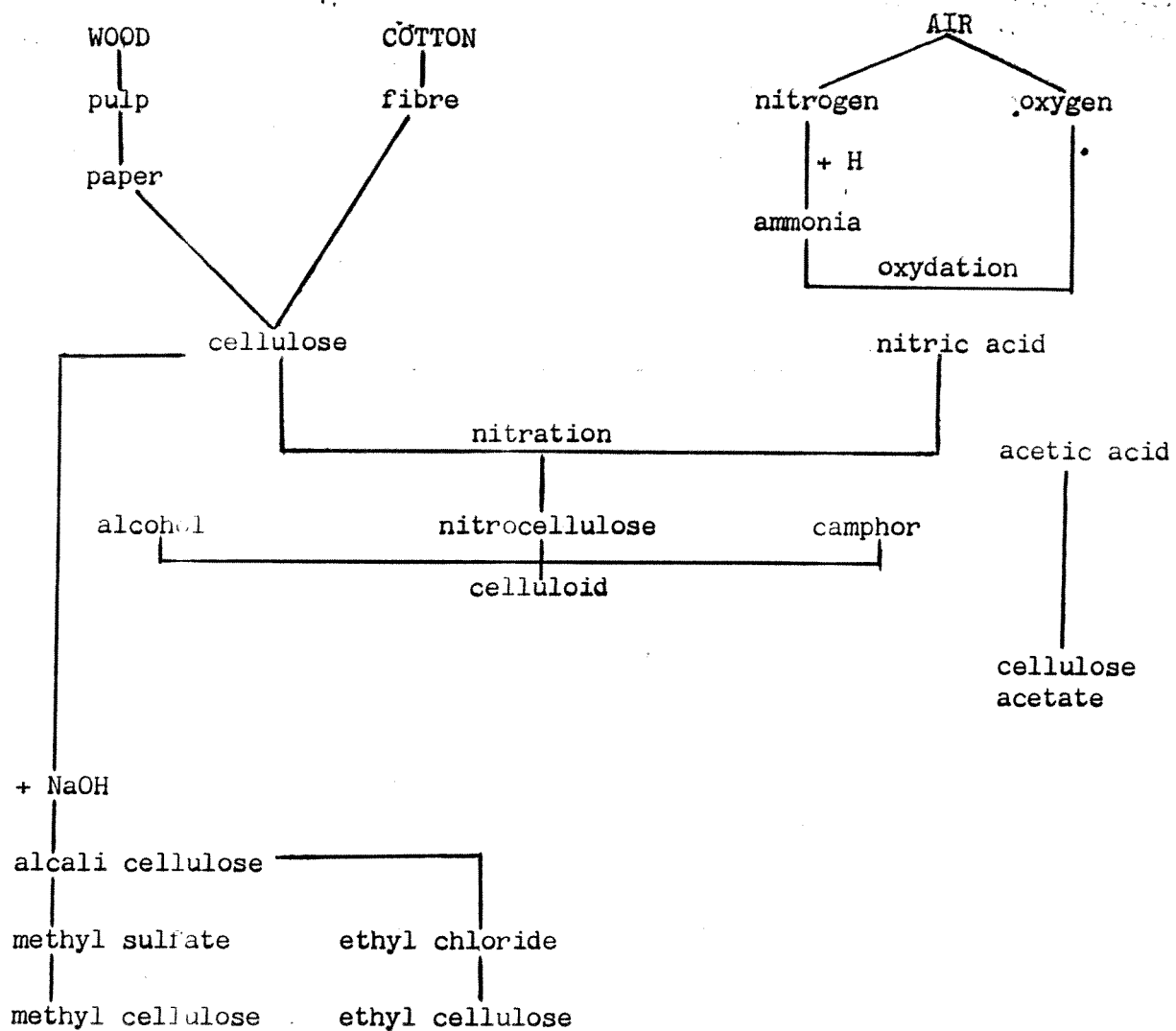
- Accelerators
- Antioxidants
- Antistatics
- Blowing agents
- pigments to give color
- and reclaim rubber

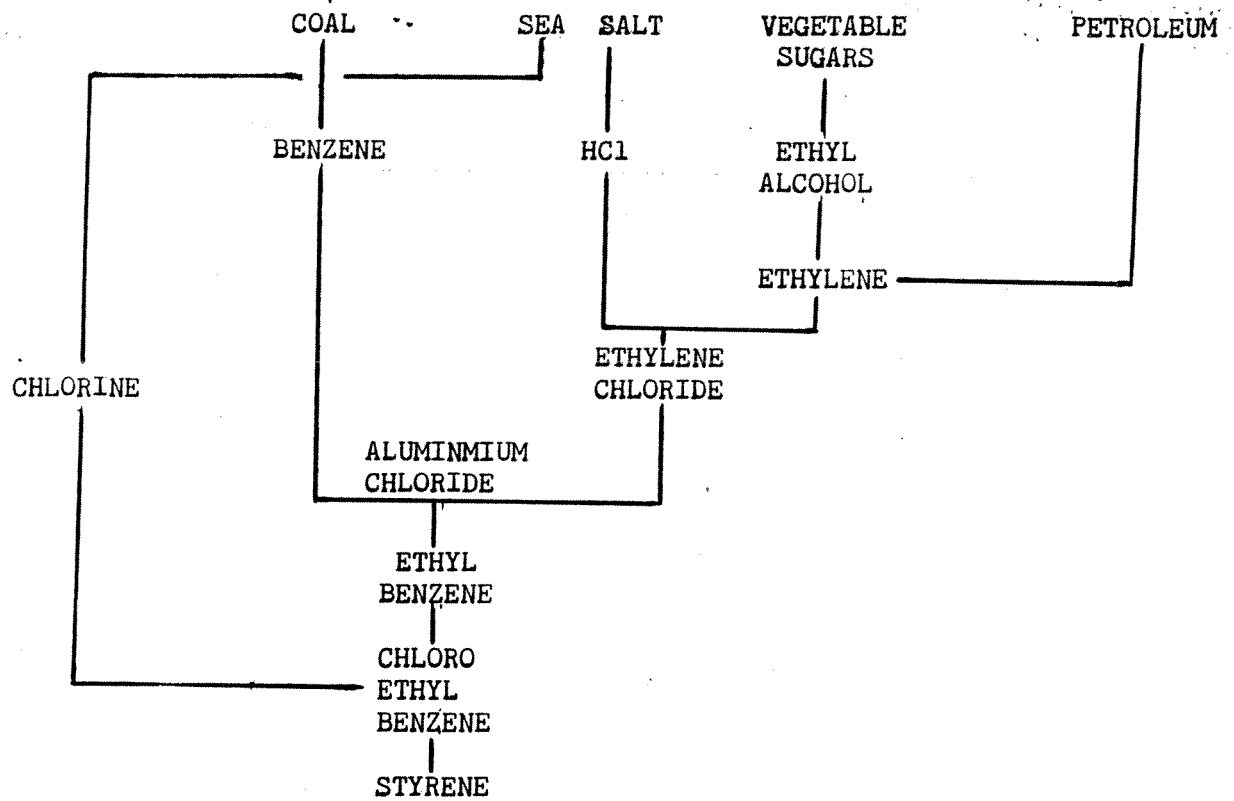
The fillers are reinforcing agents (carbon Black) or mineral agents to give weight.

To fasten the mastification process and to make it easier, mineral fats, such as paraffins, are added.

The rubber paste is ready for vulcanization and is stored with a protective layer of talc powder.

Today, natural rubber is seldom used as such but mostly blended with synthetic rubbers.





RUBBER CONSUMPTION

Tires	65%
Footwear (soolings+boots)	10%
Technical rubber	6%
Belts	4%
Isolation	3%
Textile	2%
Others (gloves, toys, etc)	10%

WORLD PRODUCTION OF RUBBER

Natural	3,093,000	55%	3,557,500	33%	3,985,000	33%
Synthetic	2,479,000	45%	7,307,500	67%	8,215,000	67%
	<u>5,572,000</u>		<u>10,865,000</u>		<u>12,200,000</u>	

Natural rubber can be used without vulcanization as CREPE.

This is a cheap material, light in weight, having self-adhesive properties but very sensitive to temperature, oils and solvents and having poor ageing resistance.

2. Cellulose is the natural material of wood, plants (cotton) or vegetable fibres.

It is the raw material for celluloid, cellulose acetates, ethyl cellulose. (synthetic fibres)

3. Casein is the protein of milk and the raw material for synthetic horn.

4. Coal, petroleum oil and natural gas are raw materials for a wide variety of synthetic elastomers and plastomers.

B. Synthetic elastomers and plastomers

1. PRODUCTION METHODS

1.1 Polymerisation

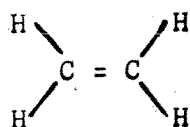
A polymer is a large molecule formed by the repeated combination of small, simple chemical units, the monomers.

It is a chemical reaction of combination of a number of similar molecules to form a large molecule.

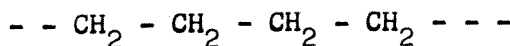
The reaction is initiated by a catalysator and needs energy.

No by-products are generated during the reaction and the building up of the macromolecule can be in a chain or a ramification, usually through the carbon links.

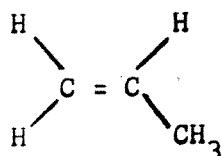
The reaction is fast and can only be controlled in given limits.



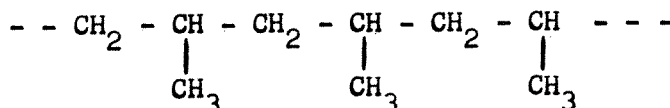
ethylene



polyethylene



propylene



polypropylene

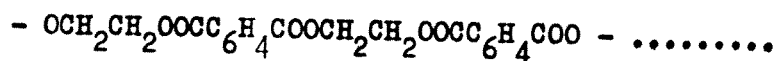
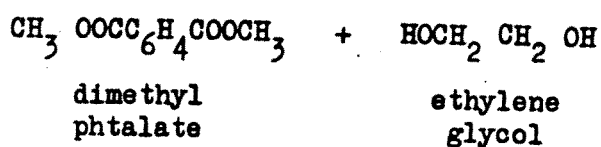
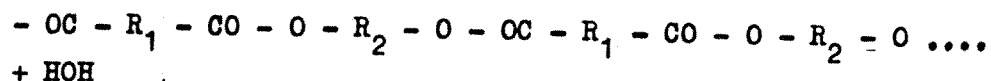
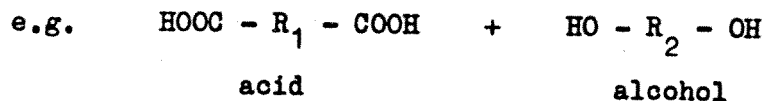
Polymers, such as polypropylene, made from only one type of monomer are known as homopolymers or addition polymers.

1.2 Polycondensation

Condensation polymers are formed from different polyfunctional monomers usually with the elimination of a smaller molecule such as water or methanol.

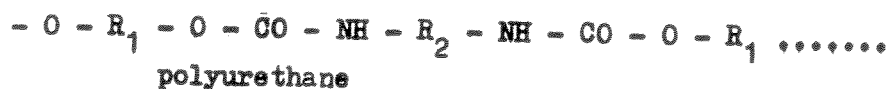
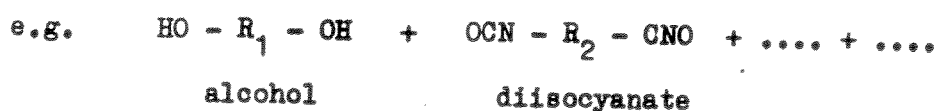
The building up of the macromolecule is not only through carbon but also through acid, nitrogen or sulfur groups.

The reaction proceeds by a stepwise intermolecular condensation, the intermediate steps can be kept for further condensation. (step reaction polymerization)

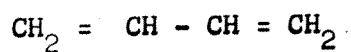


1.3 Polyaddition

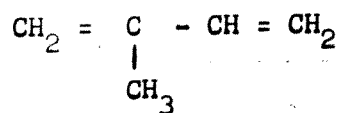
Polyaddition is the reaction of combining different macromolecules through polyfunctional links.



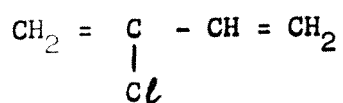
STARTING MONOMERS FOR PRODUCTION OF SYNTHETIC RUBBERS



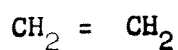
BUTADIENE



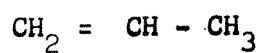
ISOPRENE



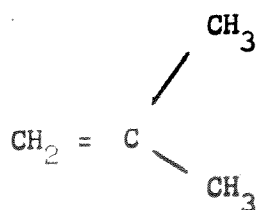
CHLOROPRENE



ETHYLENE



PROPYLENE



ISOBUTYLENE



STYRENE



ACRYLO NITRILE

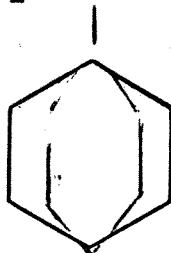
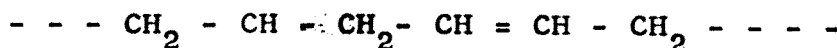
2. Types of synthetic rubbers

2.1. Butadiene rubbers

Butadiene rubber is an isoprene without methyl group



it is generally used as a copolymer with styrene



2.2. Styrene-butadiene rubber (SBR) was one of the first man-made rubber. It is comparable with natural rubber as an excellent general purpose soling material.

Pure polystyrene is a hard glassy material while pure polybutadiene is soft and rubbery. The copolymer is soft and rubbery when the polystyrene content is low, becoming harder as the proportion of polystyrene increases. Normal SBR contains about 25% polystyrene.

SBR is compounded and vulcanized in the same way as natural rubber, and is available in several quality grades. These grades differ mainly in the amounts and types of filler used. The high grades with the best wear resistance contain more of the

reinforcing fillers like carbon black or hydrated silica, and less of the cheapening fillers like soft clay and whittings. Wear resistance and flex-cracking resistance become poorer as the proportion of cheapening fillers increases.

Quite high proportions of extending oils can be used without deterioration in properties. Reinforcing fillers like carbon black reacts with the chains and become bound chemically with them, strengthening the compound. The solid fillers particles, on the other hand, are too big and weaken the compound.

Oil and solvent resistance of SBR rubber is not very good but can be improved by blending with oil resistant rubbers.

Density of SBR rubber is greater than that of natural rubber.

Unlike natural rubber, SBR and most of the other synthetic rubbers cannot be used in the "crepe" form.

There is little to choose between natural rubber and SBR as far as general wearing properties are concerned. Whether one or the other or some blend of the two is chosen depends on cost.

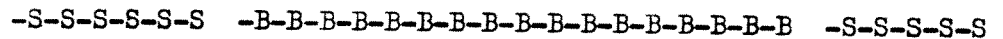
Different hardnesses are obtained by blending "high styrene" resins with the normal SBR. The harder blends are commonly referred to as "resin rubbers".

SBR in solid form is available as sheets or moulded units for soling. It can also be obtained as pre-mould blanks for direct vulcanizing process.

2.3. Thermoplastic rubber (TR)

Thermoplastic rubber is a styrene-butadiene co-polymer but it differs from normal SBR in that the monomers units are arranged in blocks.

It is a tri-block system in which a long polybutadiene chain has a shorter polystyrene chain attached to each end, as shown below



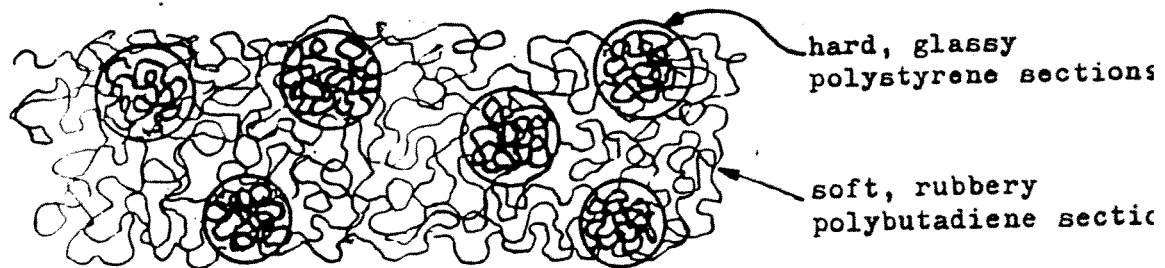
It is an addition co-polymer made by a solution polymerization technique with special catalysts. The blocks are made separately then joined together afterwards.

TR behaves very differently to the random SBR co-polymer in that it does not need to be vulcanized to give the required strength and elasticity.

It is compounded with fillers and additives but without cross-linking agent, it retains its thermoplastic nature and can therefore be processed by the much cheaper injection moulding technique. Unused or waste material can be recycled.

TR gets its strength from 'reversible' cross-links which are a unique feature of many block copolymers. These cross-links are destroyed when the material is heated to its moulding temperature and reform again on cooling.

This arises because, like oil and water, polystyrene and polybutadiene are not very compatible with each other. As the molten co-polymer is cooling, the polystyrene sections collect together separately from the polybutadiene sections.



Provided that the polybutadiene is in the greater proportion (60 % or more) it will form the continuous phase, with isolated polystyrene areas distributed amongst it.

At room temperature the polystyrene is hard, but the material as a whole is very rubbery. On stretching, the polybutadiene sections uncoil but are prevented from slipping because they are 'anchored' in the polystyrene areas.

As a soling material, TR can be compared to SBR and also to PVC.

The following are the most important properties :

1. Wear resistance
2. Slip resistance
3. Flex-cracking resistance is exceptionally good, especially at low temperatures. It remains flexible down to -50°C .
4. Oil and solvent resistance are very poor but can be improved by blending with EVA or polypropylene.

5. There are problems with adhesion of TR.

In general, PU cements work well after the TR has been halogenated.

6. Density of TR is less than PVC or SBR

7. TR is more expensive than SBR but cheaper to process.

TR can be blended with small amounts of polystyrene, EVA or recycled rubber, to increase hardness (compact TR) or with special oils to increase softness. In general the softer the TR the poorer is the wear resistance but the better is its slip resistance.

Hard solid TR can be used for top-pieces provided they are not too small, and for heel blocks provided they are not too thin-walled. This is because TR does not have very good "crepe" resistance properties.

2.4. Polyisoprene rubber

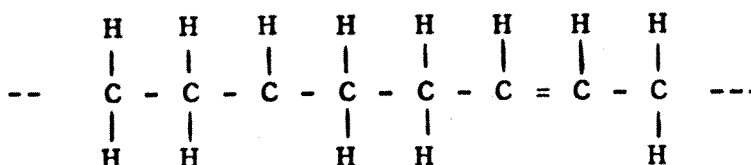
Polyisoprene rubber has the same chemical composition as natural rubber but the chains are not as long and does not have the same degree of regularity.



Physical properties are similar though somewhat inferior, but the flow properties in moulding are better. For this reason, it is often blended with SBR or NR to improve moulding.

2.5. Ethylene-Propylene Diene Modified Rubber EPDM

EPDM is a random co-polymer containing ethylene and propylene and a small proportion of butadiene.



ethylene

butadiene

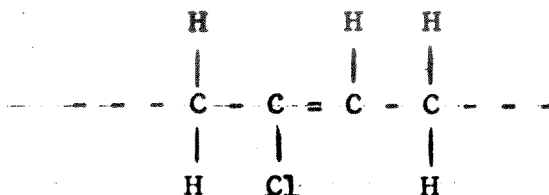
propylene

Ethylene-propylene co-polymer cannot be vulcanized with sulfur, the presence of butadiene allows such vulcanization.

EPDM is an alternative to SBR and NR as a general purpose soling material. It is lighter in weight, has good wear and flow properties. Oil and solvent resistance are poor but ageing and hear resistance are good.

2.6. Polychloroprene rubber

Polychloroprene are addition polymers which can be compounded and vulcanized in the same way as SBR.



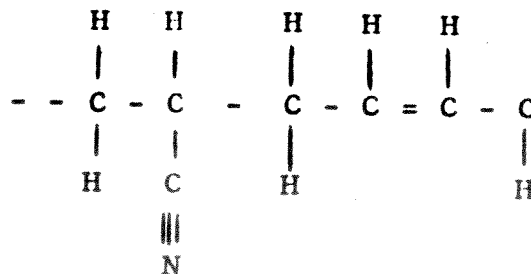
Polychloroprenes are rather expensive but have outstanding qualities :

- very hard wearing
- resistant to cut growth
- very resistant to oils
- very resistant to heat
- flame resistant
- exceptionally resistant to ageing
- slip resistant, even on oily surfaces

Their use as soling material is restricted to industrial safety footwear. Their other main use is as flexible adhesive.

2.7. Nitrile rubbers

Nitrile rubbers are addition co-polymers of acrylonitrile and butadiene.



acrylonitrile butadiene

The most important properties of nitrile rubbers are :

- exceptional heat and oil resistance
- good wear resistance
- relatively high electrical conductivity.

However, ageing, particularly to sunlight, is not so good. In general, the higher the acrylonitrile content the better is the oil and heat resistance but the poorer are the physical properties, especially the low temperature flexing. Plasticising oils can be added to overcome this last problem.

Nitrile rubbers are used as an alternative to polychloroprenes in industrial footwear.

When blended with phenolic resins, nitrile rubbers become hard and give good top-piecing material.

Co-polymerised with styrene, nitrile rubbers give Acrylonitrile-Butadiene-Styrene rubbers ABS.

Acrylonitrile gives greater oil resistance, styrene gives stiffness, while butadiene is softening. The combination of the three gives different kinds of rubber.

Formulations which are high in acrylonitrile-styrene are used for heels where greater resistance to fatigue and splitting is needed. Butadiene will improve the impact resistance and make the material more flexible.

There is the added advantage that the moulded surfaces of ABS can be specially treated to take metallic and pearlised finishes.

The main disadvantages are that ABS is very expensive and difficult to mould.

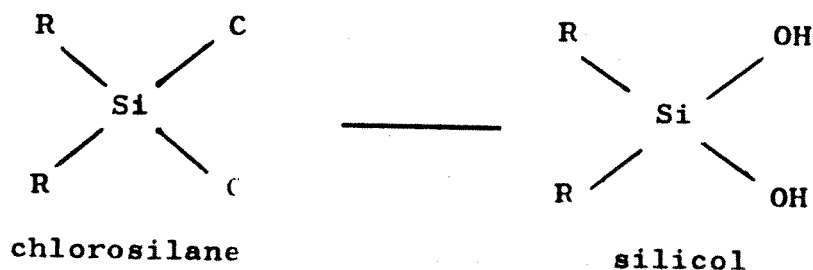
2.8. Silicone Rubbers

Because of their structure and properties, Silicone rubbers are very different from the other synthetic rubbers.

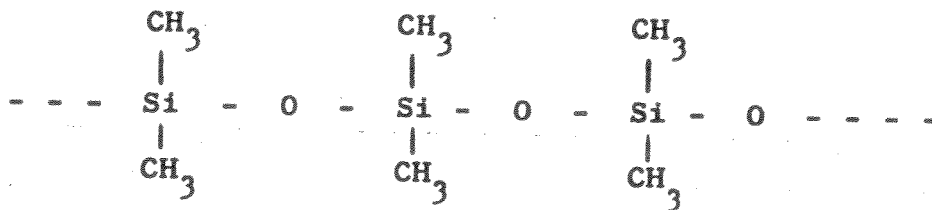
They are the only ones where the main chain of the molecule has no Carbon atoms but is a succession of Silicium and Oxygen atoms.

The production of silicone rubbers starts from a chlorosilane from which the Chlorine atoms are hydrolyzed in an alcohol.

The so obtained silicol can be polymerized by polycondensation through the alcohol groups with the elimination of water.



R is generally a methyl group CH_3



Silicone rubbers can be vulcanized by hot or cold vulcanization removing Hydrogen atoms to create free links for reticulation. Silicone rubbers are very elastic, they don't show deformation even after prolonged extension or compression. They keep their elastic properties in a very range of temperatures, from minus 50°C to plus 300°C.

Fillers and other additives can be incorporated in Silicone rubbers provided they don't modify the properties.

Silicone rubbers are very resistant to oils, ozone and U.V., they also have good electrical conductivity.

They are used to make seals, hoses, tubings. They have many applications in automobile, aircraft and satellite construction.

Silicone rubbers are not adherent. This property combined with their high elasticity and heat resistance makes from them a good material for flow moulding and printing.

2.9 Fluorine Rubbers

The most important fluorine rubber is a tetrafluorethylene where the Hydrogen atoms of the polyethylene are replaced by Fluorine atoms.



Fluorine rubbers are very resistant to low (-200°C) as well as to high temperatures ($+260^{\circ}\text{C}$). They are resistant to chemicals and have a very low dielectric constant. They are not adherent and slippery.

In the footwear industry, fluorine rubbers are used as parts of machines. (wipers of lasting machines, preforming machines, beds of stitching machines)

3. Cellular rubbers

Most of the rubbers, natural or synthetic, can be made into cellular form to reduce the weight and give better shock-absorbing qualities.

A blowing agent (organic amines N-NO) is included during the compounding. At the vulcanization temperature, the blowing agent generates nitrogen gas which makes small bubbles in the material.

The characteristic structure produced consists of fine, regular, closed cells which are not inter-connecting.

The expansion of the rubber in the mould is carefully controlled so that a solid layer of rubber for the tread surface is allowed to form first.

The degree of expansion is monitored by the percentage and the strength of the blowing agent in such a way that small or big, many or few cells are produced, giving :

- microcellular rubbers with small cells
- cellular or sponge rubbers with medium sized cells
- foam rubbers with big cells.

Wear resistance decreases but flex and slip resistance increases when the expansion increases.

If the blowing agent has not completely reacted during vulcanization, excessive shrinkage of the soles will occur if they are exposed to heat (reactivation or even in shop windows). For this reason, it is advisable to re-heat cellular rubbers a few days after vulcanization.

Foam rubbers have too low abrasion resistance and are too compressible to be used as soling materials. Their main uses are as interlinings and cushioning pads.

4. Translucent rubbers

These are materials with high rubber content and lower amount of fillers. The light color is that of the rubber or can be shaded with hydrated silica or kieselguhr.

Translucent rubbers are lighter in weight and have good wear, abrasion and flex resistance.

ANNEX

Some examples of rubber compounding formulas for soles

1. Natural rubber	Smoked sheets	100 parts
	Zinc oxide	5
	Sulfur	3
	Vulcanizing agent	1.8
	Stearic acid	1.5
	Antioxidant	1.5
	Benzoic acid	2
	Pigment (brown)	4
	Carbon black	0.25
	Kieselguhr	60
	Rubber content	55.8 %
	Vulcanization under 40 ⁵ Pa during 10 minutes	
	Shore hardness	76

2. Synthetic rubber	SBR	90 parts
	reclaim	10
	zinc oxide	3.5
	resin	8
	mineral rubber	2
	stearic acid	2
	glycol	3
	filler aluminum silicate	65
	anti-oxidant	0.5
	vulcanizing agent	2.3
	sulfur	2.5

Rubber content 54 %
Vulcanization at 150°C during 10 minutes

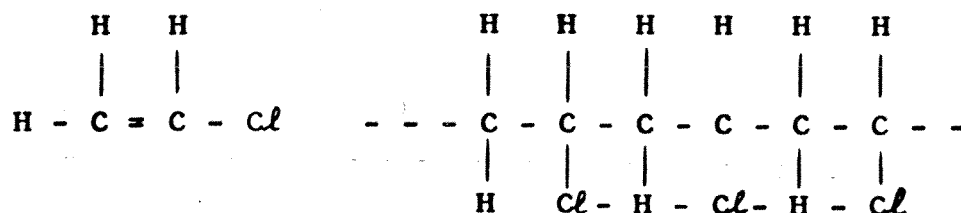
3. Translucent

	<u>soft</u>	<u>hard</u>
latex crepe	100	100
zinc oxide	0.8	0.8
sulfur	1.8	2.5
vulcanizing agent	0.6	2
stearic acid	1.5	-
paraffine	0.5	-
paraffine oil	1.5	-
triethanolamine	-	1
ethylene glycol	-	3
anti-oxidant	0.6	0.6
kieselguhr	-	40
Rubber content	93.1%	66.7%
Shore hardness	40	68
Elongation at break	845%	685%

5. Other Elastomers

5.1 Polyvinyl Chloride PVC

Polyvinyl chloride is an addition polymer made from vinyl chloride.



vinyl chloride

polyvinyl chloride

PVC is a cheap material and has many applications. It can be produced in a hard material with good corrosion and mechanical properties, or in a soft material through mixing with plasticisers (*)

PVC can be mixed with plasticisers in all proportions to increase its flexibility.

However, as the proportion of plasticiser increases, flexibility, softness and stretch increase but strength and maximum working temperature decrease. The correct choice of plasticiser, which will give enough flexibility without too much reduction in strength or other properties, is very important.

Being thermoplastic, PVC can be injected and melted back but it requires a heat stabiliser to prevent chemical decomposition during hot processes.

(Hydrochloric acid can be liberated)

PVC is never cross-linked and only small amounts of solid fillers can be added without excessive weakening. Other standard ingredients include lubricants to aid moulding and pigments for coloring. Blowing agents can be included for production of cellular structures.

The main uses of PVC in footwear are :

- injected footwear (boots, sandals, etc.)
- injected unit soles and direct injection on uppers
- coated fabrics

The advantages of PVC are :

- cheap material to buy and cheap to process
- great versatility, can be blended with plasticisers, synthetic rubbers, pigments and dyestuffs
- good flame resistance, burning PVC is self-extinguishing.

The disadvantages are numerous :

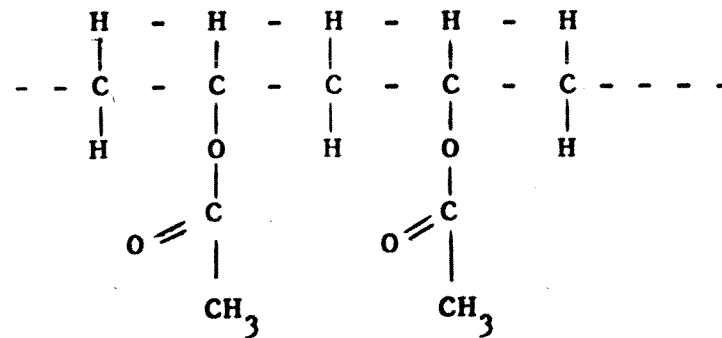
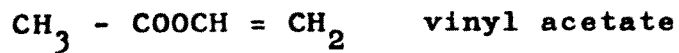
- low wear resistance of the soft grades. However this can be improved by blending with PU or nitrile rubbers. If not blended, cellular PVC cannot be used for soling.
- high specific weight
- low slip resistance, especially on wet surfaces
- very poor flex-cracking resistance in cold conditions as well as for injected footwear as for soles or coated fabrics.

* A plasticiser is a high boiling point liquid which acts as a lubricant for polymer chains, allowing them to slip over each other.

- while pure PVC is quite resistant to oils, plasticised PVC is not. Oils and solvents tends to leach out the plasticiser and cracking becomes more likely.
- polychloroprene cements does not bond well to plasticised PVC, this is because plasticiser tends to migrate to the surface of the PVC and blends with the adhesive, thus weakening any adhesive bond. PU adhesives are more resistant to plasticisers and can be used satisfactorily provided surface plasticiser is wiped away with solvent before the PU cement is applied. This is true for both PVC solings and PVC coated fabrics. Because of its thermoplasticity, PVC cannot be roughed.
- PVC articles are glossy and when pigmented, the colors are bright giving the typical "plastic" appearance.
- the inferior qualities of PVC articles are largely responsible for the consumer impression that PVC goods are "cheap and nasty". Recently developed co-polymers and blends overcome most of the problems and improve the quality of PVC.

5.2 Polyvinyl Acetate PVA

Polyvinyl acetate is an addition polymer made from vinyl acetate.



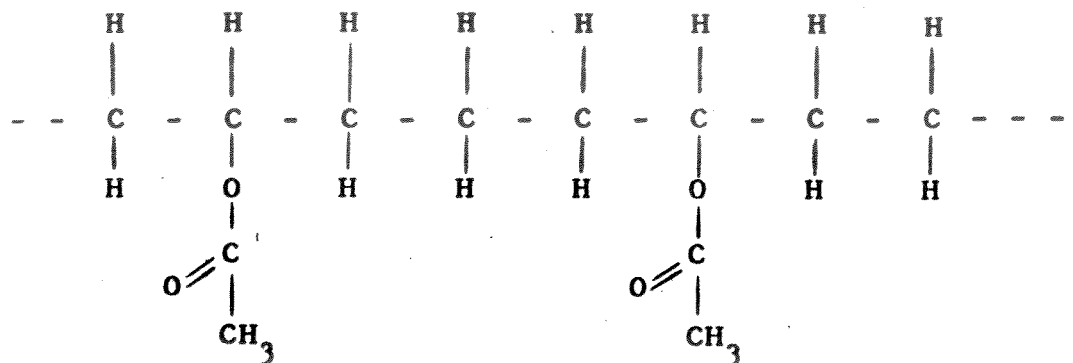
The chlorine group of PVC is replaced by acetate groups CH_3COO . PVA is not used as such in footwear materials, it can be blended with natural or synthetic rubbers.

The main utilizations of PVA are in the production of chewing gums, some adhesives and paints.

PVA and PVC can be co-polymerized between them or with methyl acrylates giving polymers that can be moulded or injected at lower temperatures.

5.3 Polyethylene Vinyl Acetate EVA

Ethylene vinyl acetate is a co-polymer of ethylene and vinyl acetate



At low concentration of vinyl acetate, up to 10 %, these co-polymer behave like polyethylene but as the vinyl acetate content is increased to 30-40 %, the co-polymer becomes progressively more soft and rubbery. The properties vary with the vinyl acetate content but, in general, the copolymers are extremely tough and remain flexible even at low temperatures.

EVA can be cross-linked with peroxides (no sulfur), blown in microcellular structure and filled.

EVA is a lightweight material which, in microcellular form, has the lowest density of all the soling materials 0.25 to 0.4, can even go down to 0.1

EVA has good flex-cracking resistance even at low temperatures. The mechanical resistance of EVA is good but the cohesion is low and the compression set not so good as cellular rubbers. Blending with TR improves the cohesion.

EVA co-polymers exhibit good resistances to acids, alkalis and many oils but are attacked by halogenated solvents, trichlorethylene and hydrocarbons such as toluene and petrol.

EVA has good ageing properties but is very sensitive to sunlight. Wear resistance can be improved by blending with SBR and/or polyethylene with silica filler.

Slip resistance can be poor on some surfaces.

EVA soles can be stuck satisfactorily with polychloroprene cement after scouring, or with special primers and PU cement. Adhesion problems are frequent due to the failure in cohesion, especially when the vinyl acetate content is less than 15 %.

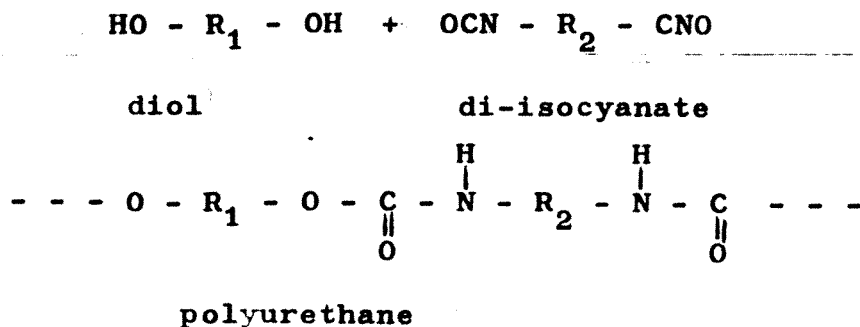
EVA co-polymers are easy to color in a broad range of shades, giving attractive colors, not too glossy and without "plastic" appearance.

EVA is considerably more expensive than PVC and some rubbers but this is compensated by its low density.

5.4 Polyurethane PU

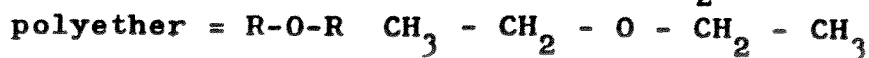
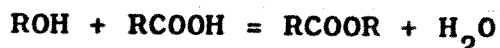
An isocyanate $R \cdot N = C = O$ can react with an alcohol $R - OH$ to form an urethane $R - NH - COO-R^1$

A polyurethane is an addition polymer made by reaction of polyalcohols and polyisocyanates



There are many polyurethanes with properties ranging from those of glasses to those of rubbers depending partly on the nature of R_1 and R_2 which may be long polyester or polyether chains. As long as the chains are linear, the PU is thermoplastic. Both polyester and polyether chains have an alcohol content in excess giving free OH groups. For a high OH content, the final polymer will be hard, for a low OH content it will be soft.

(*) polyester = alcohol + organic acid



PU can be reticulated by cross-linking giving materials in a large range of softness and hardness.

PU are used to make flexible foam products; rigid foam products; hard compact materials or elastomers; coating and paints; treads and soles; fibers, etc.

Polyurethanes have three main uses in the footwear industry : soling materials, coatings for upper fabrics and adhesives.

In the tanning industry polyurethanes are used in the finishes, namely for patent leather. They are also used for grain impregnation.

The majority of solings are made by a process called reaction moulding in which the polymerization takes place partially or wholly in the mould. Gases released during the reaction create a cellular structure. The gas forming comes from the reaction between the isocyanate and water giving CO_2 that becomes trapped in the reaction mixture and foams the polymer



There are two types of cell structure which can form, a closed and a large cell structure.

Polyester based PU's tend to give the closed cell structure similar to cellular rubber with a thin outer skin, while polyether based PU's tend to give the open structure which has larger cells and a relatively thick outer skin. Some of these cells are interconnecting and therefore water absorbent. Silicone oils and pigments are added to the reaction mixture but fillers are not used.

Polyurethanes can also be injected on special adapted machines.

PU is perhaps the best all-round soling material on the market, its important properties include :

- excellent wear resistance. In its cellular form it is as good as many compact rubbers.
- very good resilience, good shock absorbing properties
- very low density
- good slip resistance
- very good oil resistance
- good adhesion with PU cements. No adhesive is needed when direct moulding to leather uppers
- excellent cut-growth resistance, flex cracking is usually satisfactory
- ageing resistance is good but heat and flame resistance are low
- polyurethanes generally are liable to chemical breakdown in wear by hydrolysis, but polyether based types are the more resistant to this. Hydrolysis is much more a problem with PU coated fabrics than with soling. The usual result is cracking of the PU film followed by delamination from the fabric base.
- some free components existing in the PU can migrate and attack nitrocellulose finishes causing discolorations. It is recommended to avoid the use of nitrocellulose finishes on leather or soles when the soling material is PU.

- PU are sensitive to polar organic solvents. Ketones, esters or alcohols should not be used for cleaning or polishing.
- Processing of PU, especially polyester is difficult, needs high accuracy, care and control. The life time of the components is very short.
- PU are expensive.

6. Plastomers

6.1 Polystyrene

Styrene or styrolene is one of the oldest raw materials for the plastic industry (1830-39).

Styrene, $C_6H_5CH = CH_2$ can be polymerized with itself to form an addition polymer polystyrene or with many other materials to form copolymers.

The chains of polystyrene are not regular in shape or flexible at room temperature so that the polymer is brittle.

If 5 to 10 % polybutadiene is added to the styrene monomer before polymerization, the product is still hard but has much better impact resistance. This modified polystyrene becomes "high impact polystyrene" HIPS. The polybutadiene becomes dispersed in the polystyrene as tiny rubbery particles which can be deformed under impact and absorb shock. HIPS has very good moulding properties and is extensively used for heels, last, wedges and platforms. These components need to keep their shape under prolonged pressure and must resist being split by heel pins.

Polystyrene and HIPS are attacked by the solvents used for many sprays and adhesives. Consequently spray finishes and material coverings for heels adhere well but excessive use of solvent should be avoided.

Polystyrene is also used for impregnation of fabrics for toe puffs and stiffeners of both the heat-activated and solvent-activated types. Although hard, they lack the resilience of other types and soften with use.

6.2 Acrylonitrile-Butadiene-Styrene ABS

ABS is an addition co-polymer made by polymerization of styrene and acrylonitrile monomers to which some SBR or polybutadiene has been added.

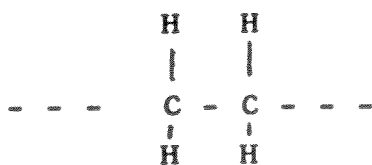
Acrylonitrile gives greater oil resistance and stiffness, styrene gives stiffness while the rubber becomes dispersed in the same way as in HIPS to give even better impact resistance.

Formulations which are high in acrylonitrile are used for heels where greater resistance to fatigue and splitting is needed.

There is the added advantage that the moulded surfaces of ABS can be specially treated to take metallic and pearlescent finishes.

ABS is much more expensive than HIPS and more difficult to mould. Formulation with more polybutadiene are more flexible and have been used for certain types of filmic toe puffs.

6.3 Polyethylene PE



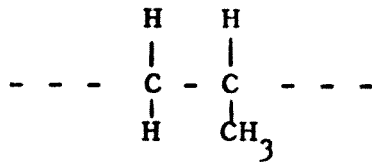
This is an addition polymer made from ethylene monomer (gas).

There are two polymerization methods used. One is carried out at high pressure, and the other at low pressure using a special catalyst system.

Low Density Polyethylene LPDE, made by polymerization at high pressure; has chains with many branches and the degree of crystallinity is only 55 - 70 %. It is used for stiffness and insoles and for foam insoles when blended with SBR. It is a cheap material.

High Density Polyethylene HDPE, made by polymerization at low pressure has chains with fewer branches and the degree of crystallinity is higher at 75 - 90 %. It is stronger, stiffer and harder. It also has a higher maximum working temperature. Its main use is in lasts.

6.4 Polypropylene PP

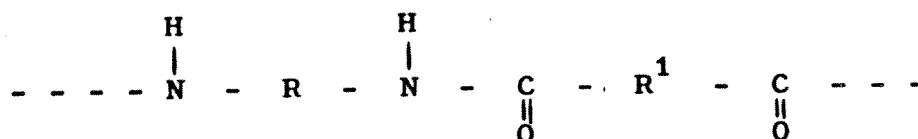


Polypropylene is very similar to HDPE both in chemical and physical properties. It is slightly stiffer and harder but low temperature flexing properties are not so good. Its maximum working temperature is higher and the density lower than that of LDPE.

Main uses include : heels

composite insoles. Cellulose board insole splitted from heel to waist parallel to the top and bottom surfaces. Molten PP is forced into the split and the whole insole is moulded to the bottom of the last. The PP gives a firm seat and eliminates the need for a shank.
ladies heel top pieces
soling for some sport shoes
fibres (poromerics)

6.5 Polyamides



Polyamides are alternating co-polymers made by condensation polymerization. There are many polyamides in which R and R¹ vary. The best known is Nylon 6,6 in which R is (CH₂)₆ and R¹ (CH₂)₄

There are other types of nylons.

The nylons are an important group of polyamides in which the chains are very regular in shape with no branches. The attractive forces between the chains are very strong so that a high degree of cristallinity is possible. The nylons are therefore strong, hard and very tough materials. They have a good wear, oil and solvent resistance. Finding a suitable adhesive can be a problem and special primers are needed.

Polyamides are widely used for fibres in sewing threads and fabrics (woven, non-woven or knitted)

They can be used for heels and for hard wear resistant soles for some sport footwear, but adhesion problems and poor slip resistance make them unsuitable as a general soling material.

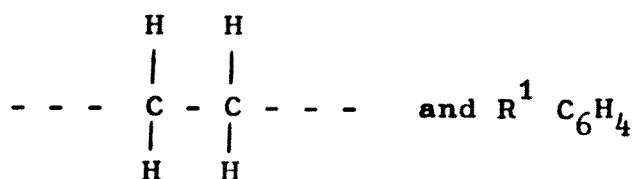
Polyamides are often used for certain bearings and gear wheels in machinery with the advantage that no lubrication is needed.

Polyamides are extensively used as hot-melt adhesives.

6.6 Polyesters



Like the polyamides, there is a whole series of polyesters of which one of the best known is "Terylene" (I.C.I.) where R is a polyethylene



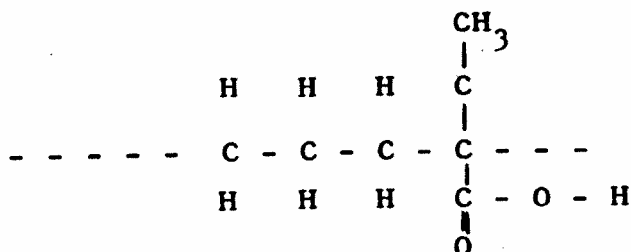
Polyesters are also alternating co-polymers made by condensation polymerization. They also have regularly shaped chains with no branches and strong attractive forces. The properties and uses are very similar to the polyamides, fibres and hot melt adhesive mainly.

There is also a polyester-polyether block polymer which is thermoplastic and rubbery in properties and does not need to be cross-linked (similar to TR). This material is used for special application, especially where low temperature flexibility is needed e.g. ski boots.

6.7 Ionic Co-polymers (Ionomers)

This is a series of polymers in which a monomer such as ethylene is co-polymerized with a smaller quantity of an acidic monomer such as methacrylic acid by an addition type process.

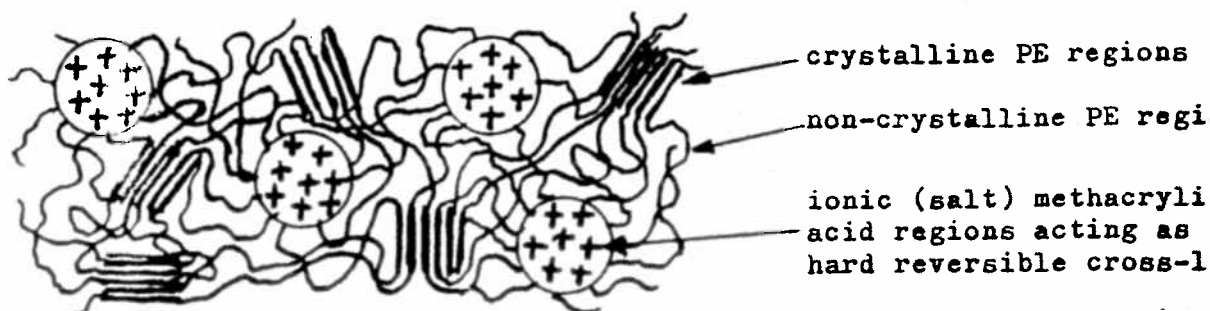
The acidic monomer is capable of forming a salt structure when ions of metals such as zinc Z^{++} , sodium Na^+ or lithium Li^+ are added.



methacrylic acid unit

In the solid polymer, the polyethylene sections form a partly crystalline and partly coiled chain structure while the acidic units gather together in separate regions. When the metal ions have been added, they enter the acidic regions to form the hard salt structure which then act as reversible cross-links.

When the co-polymer is heated, the salt structure disperse and the material melts and can be moulded. On cooling the structure reforms.



These materials have the toughness of HDPE and strength and low temperature flexing properties, but have much better resilience. They resist the softening effect which repeated flexing has on many other types of elastomeres. They can be made into very resilient foams.

Main shoe trade include filmic toe puffs, foam insocks, platforms top pieces and some sport shoe solings.

Some recent developments in elastomers/plastomers

1. Materials
 - expanded PVC with density of 0.6
 - PVC nitrile rubber compounds
 - thermoplastic PU
 - PVC/thermoplastic PU reticulated compounds
 - rubber/PU compounds
 - new types of thermoplastic rubbers
2. Machines
 - injection machines for bi and tridensity compounds
 - tricolor injection machines
 - robots for roughing
 - robots for cleaning of moulds
3. Problems
 - temperature regulation on moulds and lasts
 - bonding difficulties mainly with fabrics due to humidity or presence of starch
 - high cost of moulds

SOME ABBREVIATIONS FOR POLYMERS

ABS	acrylonitrile butadiene styrene
CA	cellulose acetate
EC	ethyl cellulose
EPE	epoxy resin ester
MBS	methyl methacrylate butadiene styrene
MC	methyl cellulose
MPF	melamine phenol formaldehyde
PA	polyamide
PNA	polyacrylonitrile
PE	polyethylene
PIB	polyisobutylene
PP	polypropylene
PS	polystyrene
PU	polyurethane
PVC	polyvinylchloride

SOME COMMERCIAL BRANDNAMES OF SYNTHETICS

Nylon	polyamide	Du Pont de Nemours	USA
Neoprene	polychloroprene	Due Pont de Nemours	USA
Perlon	polyamide	Bayer	West Germany
Rilsan	polyamide	Rhone Poulenc	France
Baypren	polychloroprene	Bayer	West Germany
Perbunan	synth. rubbers	Bayer	West Germany
Dynel	copol. PVC PAN	Union Carbide	USA
Dacron	polyester	Du Pont de Nemours	USA
Trevira	polyester	Hoechst	West Germany
Diolen	polyester	Glanzstoff	West Germany
Terylene	polyester	ICI	England
Coulene	polyethylene	Courtaulds	England
Cariflex	thermoplastic R	Shell	USA
Hycar	synth. rubbers	Goodrich	USA
Butaprenes	synth. rubbers	Firestone	USA
Vulkollan	synth. rubbers	Bayer	West Germany
Perbunan	synth. rubbers	Bayer	West Germany
Kapro	polyamides	--	Russia
Silastic	silicone rubbers	Dow Corning	USA
Siloprene	silicone rubbers	Bayer	West Germany
Silicostes	silicone rubbers	ICI	England

