

FUNCTIONAL FINISHING

The chemical structure of natural, artificial or synthetic fibres determines some of the properties that are naturally present also in finished products. Some fibres (such as linen, hemp, silk, nylon, polyester) are stronger than others (wool, viscose, acrylic) according to more or less controlled distribution of macromolecules in the polymer mass, structure stiffness and any possible inter and molecular interaction between the chains; other fibres tend to distort when stretched (cotton, viscose), and others recover their original shape after being distorted (wool); some others easily burn (cellulose), burn slowly and self-extinguish (wool, silk) or burn and melt (synthetic fibres). The above mentioned characteristics and many others make up positive and negative properties of a textile material, which must be accurately considered in view of their final application. The textile product final application will be considered from many points of view: wearability, hand, mechanical resistance, wettability, washability, deformability, fire-proof ability and many others.

The word “textile finishing” defines a series of processing operations applied to gray fabrics to enhance their appearance and hand, properties and possible applications. The term “finishing” includes all the treatments applied to gray fabrics such as scouring, bleaching, dyeing or printing while we will use the term “functional finishing” with reference to all the mechanical or chemical finishing operations carried out on fabrics already bleached, dyed or printed to further enhance their properties and possibly add some new ones.

The terms “finishing” and “functional finishing” are therefore similar and both play a fundamental role for the commercial excellency of the results of textiles, strictly depending on market requirements that are becoming increasingly stringent and unpredictable and permit very short response times.

Depending upon the type of textile substrate to be treated (staple, yarn or fabric) functional finishing processes are carried out using different means:

Mechanical means: involving the application of physical principles such as friction, temperature, pressure, tension and many others.

Chemical substances involving the application of synthesis or natural chemical products, which bind to the fibres more or less permanently

Combined mechanical and chemical means involving the application of both chemical and mechanical processes

The main purposes of functional finishing processes are the following:

- Develop the "product finishing" in all its fundamental elements such as hand and appearance;
- Give the finished fabric some properties that grant an optimum behaviour during the making-up and all through the life of the textile.

The parameters influencing the choice of the most suitable finishing process are the following:

- Fibre nature or fabric to be subjected to functional finishing treatments
- Final application of the fabric to be subjected to functional finishing treatments

Mechanical Finishing Treatments

Mechanical finishing processes can be referred to as those processes generally carried out on open-width dry fabrics, with or without heat application, which give the fabric good dimensional stability (shrink proof and shape retention) and modify the "hand" of the textile product by altering its structure (at least its surface structure)

Dry finishing

- Calendering:** a lustrous, dense and compact appearance can be obtained by means of friction, pressure and heat.
- Ciréing:** this calendering operation is carried out using special calenders and exploiting the combined actions of heat, friction and polishing agents.
- Embossing:** this particular type of calendering process allows engraving a simple pattern on the fabric.
- Sueding:** thanks to this process, the fabric has a much softer hand and an improved insulating effect thanks to the fibre end pulled out of the fabric surface. This process is carried out by means of a roller coated with abrasive material.
- Raising:** the fibre end pulled out to the fabric surface imparts an insulating effect. This process is carried out by means of hook-needles running in different directions on the fabric.
- Shearing:** the fibre ends on the fabric surface are cut by using special cutting tools.
- Singeing:** the fibre ends pulled out to the fabric surface are burnt by means of a flame (see preliminary treatments).

Wet finishing

- Wet calendering:** this process is quite similar to the dry one. The only difference is the use of steam.
- Fulling:** the structure, bulk and shrinkage of wool are modified by applying heat combined with friction and compression.
- Sanforising:** the fabric is given an optimum dimensional stability by applying mechanic forces and water vapour.
- Decating:** the lustrous appearance of the textile material is eliminated, the surface is smoothed and the fabric is given an optimum dimensional stability thanks to the action of dry or overheated saturated vapour.

Calendering

This non-permanent mechanical finishing treatment is applied to fabrics made of cellulose, protein and synthetic fibres, by means of a calender. This machine generally includes one or a series of couples of rollers pressed one against the other with adjustable pressure and identical or similar tip speeds. The cloth passes through one or more couples of rollers, which exert a smoothing and a pressing action. Some rollers are stiff while some others are made of softer material. Stiff rollers are generally made of steel or hardened cast iron and the surface can be chrome-plated, nickel-plated or made of stainless steel and can be subjected to treatments that give:

- a matt appearance similar to the abrasive blasting;
- a cross-stripe engraving to improve the fabric resistance to sliding;
- a very thin diagonal stripe patterning with silk-sheen appearance;
- a patterned engraving with embossed effects.

The fabric passing through the rollers of the calender is subjected to a very uniform pressure all along its width; if the rollers rotate at a different speed, a vigorous friction effect is generated.

Steel rollers may be equipped in such a way to be heated from the inside by means of steam, circulating fluids or electrical power. They are supported by a vertical central frame made of steel, having the same size of rigid rollers, while the surface is coated with softer material like cotton (to stand high temperatures), wool paper (to enhance the glaze finish), or jute, wool or plastic material such as polyamide.

The rollers coated with paper/wool, containing 45-50% of wool, feature good elasticity and excellent resistance to wear and are suitable for a wide variety of applications; they can also be used in embossing calendering units.

Rollers made of paper/cotton, are used almost in friction calenders and for treating "hard" fibres, thanks to their high resistance capacity. Cotton rollers, featuring higher elasticity than the paper ones, are mainly used for cotton and blends finishing and for a final full hand effect.

The life of cotton-polyester or polyamide rollers is considerably longer; in fact they are very resistant and cannot be easily etched by the passage of creases, knots or sewing. Thanks to their improved hardness, they produce on the fabric a particularly lustrous appearance and allow higher operating speeds.

The effects on the cloth can be set permanently by using thermoplastic fibres or by applying suitable (thermosetting resin or reactive-based substances) finishing products.

The use of different types of calenders gives different effects such as:

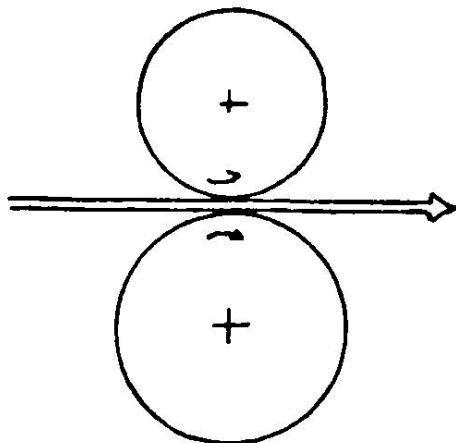
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|------------------------------------|---|
| Sheen appearance: | it can be obtained by smoothing the cloth surface, which ensures a better reflection of light. |
| Better coverage: | it is due to the compression of the cloth, which generates a flattening of each single yarn. |
| Softer hand: | it is obtained thanks to a slight ironing effect, which produces a smoother, and softer cloth surface. |
| Surface patterns: | they can be obtained by means of special effects ("embossing" for example) for decorative purposes or to modify the surface smoothness. |
| Yarn swelling and rounding effect: | they give a modest glaze finishing to the fabric, a surface smoothness and above all a full and soft hand. |

The main types of calendaring units are:

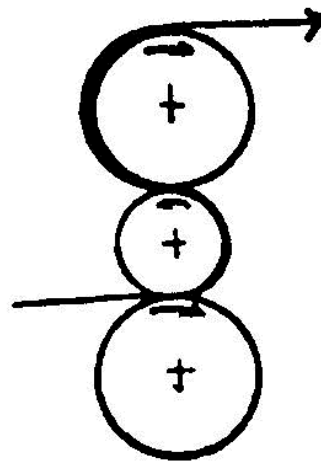
Two-roller calenders: they are made up of a smooth roller coupled with a metallic one, which can be heated. The tip speeds of the two cylinders can be different: this system architecture produces a certain friction, which gives a high glaze effect to the fabric. The lustrous effect depends on the different rotation speed, pressure and temperature.

Three-roller calenders: the most common combinations are the following:

- smooth-steel-smooth rollers: this structure allows a better lustrous effect and gives the cloth more bulk.
- steel-smooth-smooth rollers: this combination allows different effects. When the cloth passes through smooth rollers a matt appearance is given to the cloth together with fuller hand.



Picture 116 - Two-roller calender



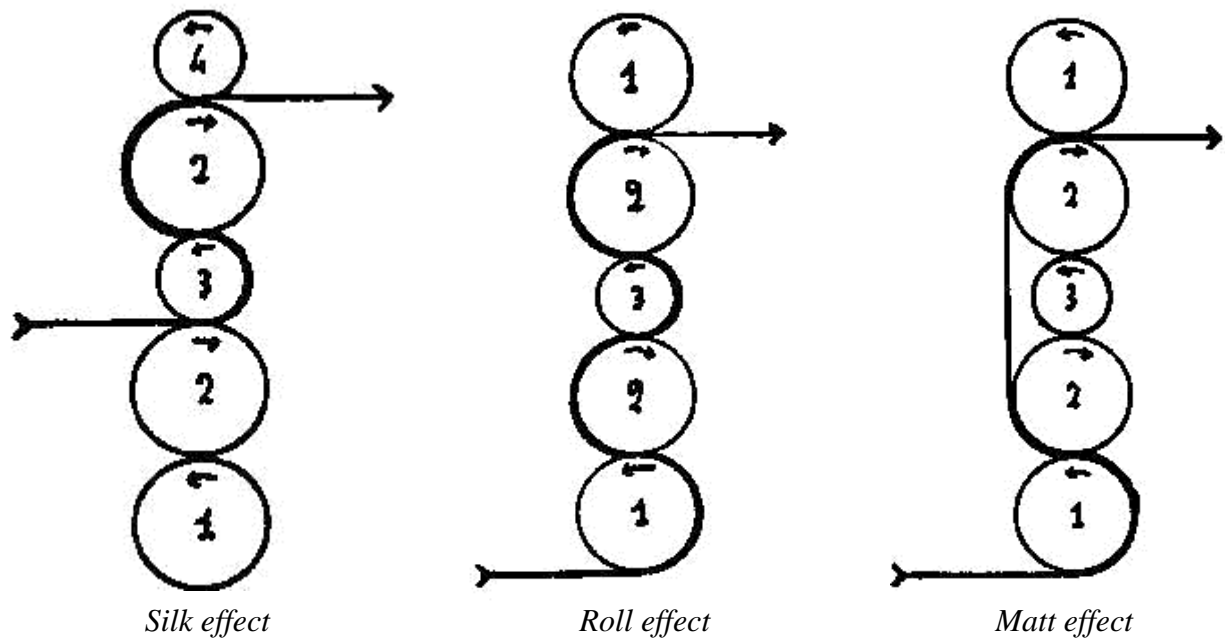
Picture 117 - Three-roller calender

Universal calenders: these calenders, equipped with 3-5-7 or even more rollers, are referred to as universal calenders. They can give the fabric different effects; some of them are detailed below:

- roll effect: flattened fabric, high coverage ratio, soft hand and moderate glaze;
- matt effect: high coverage ratio, soft hand and matt effect;
- lustrous effect: this effect originates from friction created during the passage between a smooth and a steel roller.

Mercerising-like calenders: by means of a high pressure (300-400 Kg/cm²) and temperature, applied during the passage of the cotton cloth (which is still wet when passing through the rollers) a highly glazy effect can be created, similar to the one obtained with the mercerising process.

Silk calenders (silky effect): the silky effect is obtained by feeding the cloth between a steel roller engraved with very thin diagonal stripes and a paper, cotton or rubber roller. Satin or poplin fabrics are generally treated with this type of calender. The engraved cylinder can be headed to enhance the modification of the fabric surface.

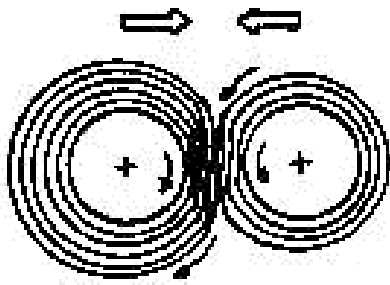


Mangling calenders: they exert a strong pressure on a cloth wound in rolls. The effect of such a pressure between the yarns leads to an accentuated rounding of the yarn with a subsequent increase of the fabric density and a highly lustrous finish. Mangler calendering can be carried out by feeding the wound cloth between two or three cylinders, which exert a powerful pressure by an alternating rolling-off and rewinding motion. This treatment is particularly valuable for pure linen or linen blend fabrics, which can be subjected to pressures up to 40 t.

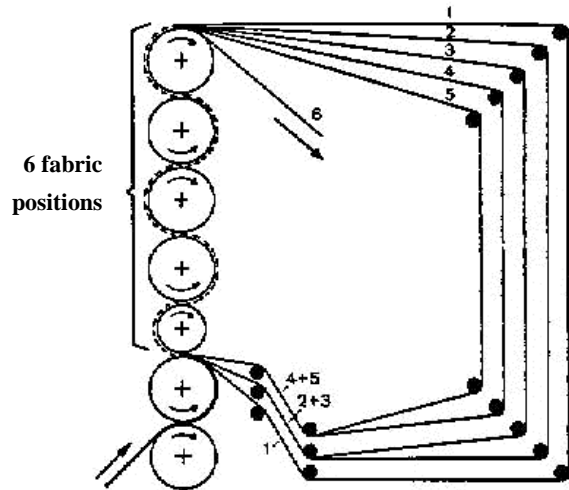
Chaising calenders: the arrangement of rollers in chaising calenders allow the fabric to be wound several times inside the calender in a number of layers ranging from 5 to 13. In this way the pressure is not exerted directly by the flat surfaces of the cylinders but by the fabric itself. The warp and weft yarns carry out a progressive rounding action; the result is a precious lustrous effect, a more bulky, full and compact hand, similar to the one obtained with mangling calenders.

Raising calenders: these calenders are used for finishing wool fabrics. They are made up of a single roller on which a metal raisers is pressed. The metal raising device envelops almost half of the whole circumference of the roller. This special calendering process gives a good lustrous effect, obtained by friction and by a moderate pressure exerted on the fabric.

Moiré effect: this attractive effect can be produced by means of a process that is essentially one of minute surface embossing or pressing of a fabric with crenellated, or ridged rollers. The pattern is imprinted on the raised filling yarns and the luster is produced by the divergent reflection of light on the lines impressed on the patterned design. This effect can be preferably given to silk, Rayon, wool, and linen fabrics. A good Moiré effect can be with fabrics with coarse weft yarns and fine warp ones.



Picture 118 – Winding-unwinding mangler



Picture 119 - Chaising calender

Embossing

Embossing is a particular calendering process through which a simple pattern can be engraved on the cloth.

The embossing machine is made up of a heated and embossed roller made of steel, which is pressed against another roller coated with paper or cotton, its circumference being exactly a whole multiple of the metal roller. A gear system drives the harmonised motion of the rollers, preventing them from sliding and granting a sharp engraving of the patterned design. After being engraved, the pattern can be stabilised by means of an appropriate high-temperature treatment or by applying suitable starchy substances.

Sueding

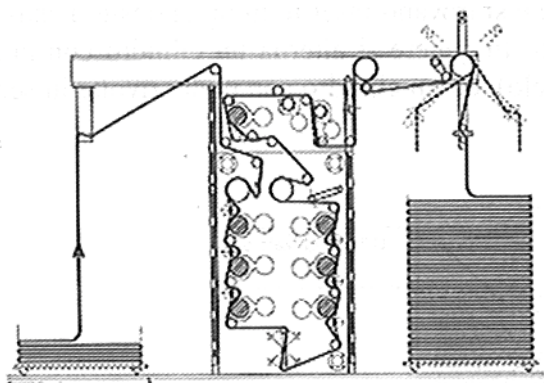
This operation is often carried out before the raising process to reduce the friction between the fibres making up the cloth and consequently to facilitate the extraction of the fibre end.

The sueding process is carried out on both sides of the fabric and modifies the appearance and the final hand of the cloth; when touched it gives a soft and smooth sensation similar to the one given by a peach-grain surface.

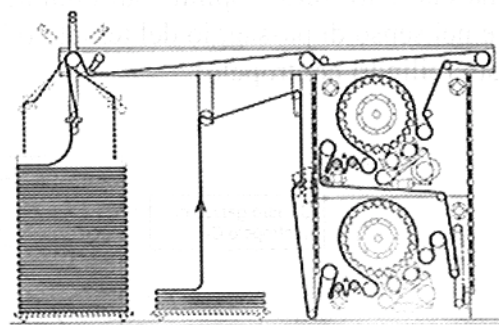
The sueding machine is made up of some rotating rollers coated with abrasive paper, which emerse the cloth and produce a more or less marked effect depending upon the pressure exerted on the fabric by the abrasive rollers. The abrasive paper used can vary according to the desired sueding degree and must be replaced after a given number of operating hours, or when it does not properly carry out suitably the sueding function. In some cases, it is possible to use also metal rollers with the surface coated with uneven and rough grains or pumice rollers performing an excellent sueding action on both dry or wet fabrics. For a very superficial sueding, the natural abrasive power of pumice can be applied with successful results.

Gray fabrics as well as dyed ones can be subjected to the sueding process; the cloth to be emersed must be completely free from any finishing resin or adhesive substance remaining on the fabric surface after desizing. The sueding process reduces mechanic and dynamometric resistance of the fabric, thus making it more subject to tearing and seaming.

The fabric can run at different speeds inside the sueding unit; a smooth pressure is kept thanks to two balancing arms assembled at the entry and at the exit of the unit. The pieces of cloth must be sewn with abrasion-resistant material such as polyester or nylon. The gears must be suitably cleaned with compressed air jets since the presence of pile residues could clog the ball bearings or drop again on the fabric surface thus creating some problems with dyeing machines filters. The sueding process, which can affect the fabric with a very wide range of effects, can give some problem when applied to knitted tubular goods but it's widely used on woven fabrics with different weights and weaves (its application ranges from coarse jeans cloth to light and delicate silk or microfibre, coated fabrics and imitation leather).



Picture 120 – A 6-cylinder sueding machine



Picture 121 –A 24-cylinder sueding machine

The sueding unit is equipped with 6 rollers performing the sueding action on the face of the fabric and 1 roller performing its action of the back of the fabric; an advantage of this system is the possibility to use sueding cloths with different grains on each single roller. Thanks to three dandy rollers, the sueding action can be automatically adjusted during the fabric processing thus allowing the sueding process to be carried out also on knitted goods.

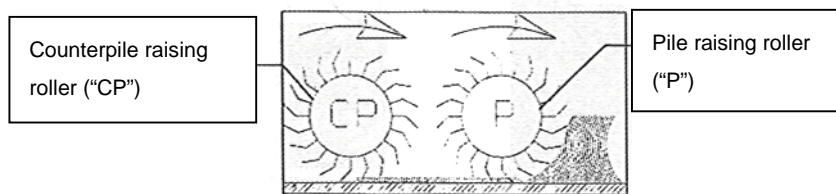
The 24-roller sueding unit assembled on 2 rotating drums features some advantages if compared to traditional machines equipped with 4-6-8 rollers: the combined action of several rotating rollers and the beating effect grant a smooth sueding, and a much softer hand than any other machine; no differences are generated between the centre and the selvedge; no stripes are formed on the fabric; the wide contact surface allows very high operating rates. The great number of moving rollers performs a gentle action on each single sueding roller thus granting the maximum sueding smoothness. Furthermore the life of the abrasive cloth is much longer than the one assembled on conventional machines. In fact, 100,000–150,000 meters of synthetic fabric and up to 200,000–250,000 meters of 100% cotton fabric can be processed in standard processing conditions before replacing the abrasive; sueding units can also be transformed into raising (napping) units by assembling a special conversion kit.

All sueding machines are equipped with a brushing unit assembled at the exit to reduce the powder resulting from the sueding process.

Raising (Napping)

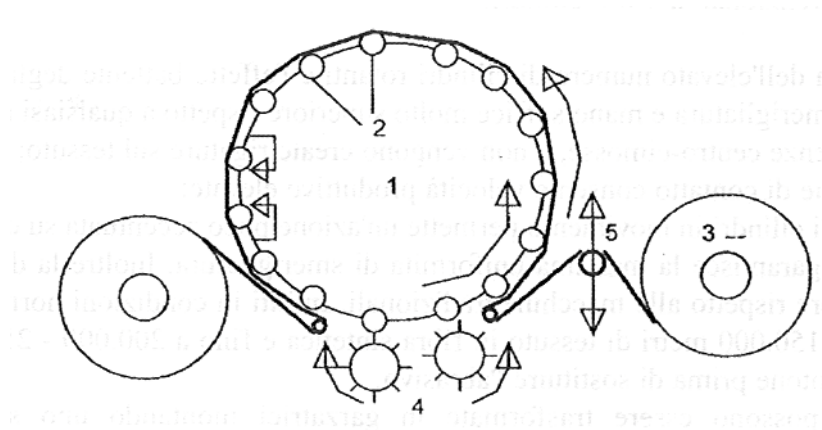
The raising process is a very old technique known also to Romans (as pictured in some paintings found in Pompeii). This operation is particularly suitable for wool and cotton fabrics; it gives a fuzzy surface by abrading the cloth and pulling the fibre end to the surface. During those last years this process has also been applied on polyester/viscose blends and acrylic fabrics.

By means of this process a hairy surface can be given to both face and back of the cloth providing several modifications of the fabric appearance, softer and fuller hand and bulk increase. This enhances the resistance of the textile material to atmospheric agents, by improving thermal insulation and warmth provided by the insulating air cells in the nap. The fuzzy surface is created by pulling the fibre end out of the yarns by means of metal needles provided with hooks shelled into the rollers that scrape the fabric surface. The ends of the needles protruding from the rollers are 45°-hooks; their thickness and length can vary and they are fitted in a special rubber belt spiral-wound on the raising rollers. These rollers are generally alternated with a roller with hooks directed toward the fabric feed direction (pile roller), and a roller with the hooks fitted in the opposite direction (counterpile roller).



Picture 122 - Raising rollers

The machine also includes some rotating brushes, which suction-clean the nibs in pile and counterpile directions. Actually the trend goes towards a ratio of raising rollers/pile rollers equal to 2 or 1/3. The two series of rollers have independent motion and can rotate with different speed and direction thus carrying out different effects.



Picture 123 – Raising (napping) machine: 1: roller; 2: rollers equipped with hooks; 3: fabric; 4: nib cleaning brushes; 5: fabric tension adjustment

The action of these systems is almost powerful and the results depend upon the effects and the type of fabric desired .

The raising effect can be obtained by adjusting the fabric tension (5) or by adjusting the speed and the roller rotation direction (2).

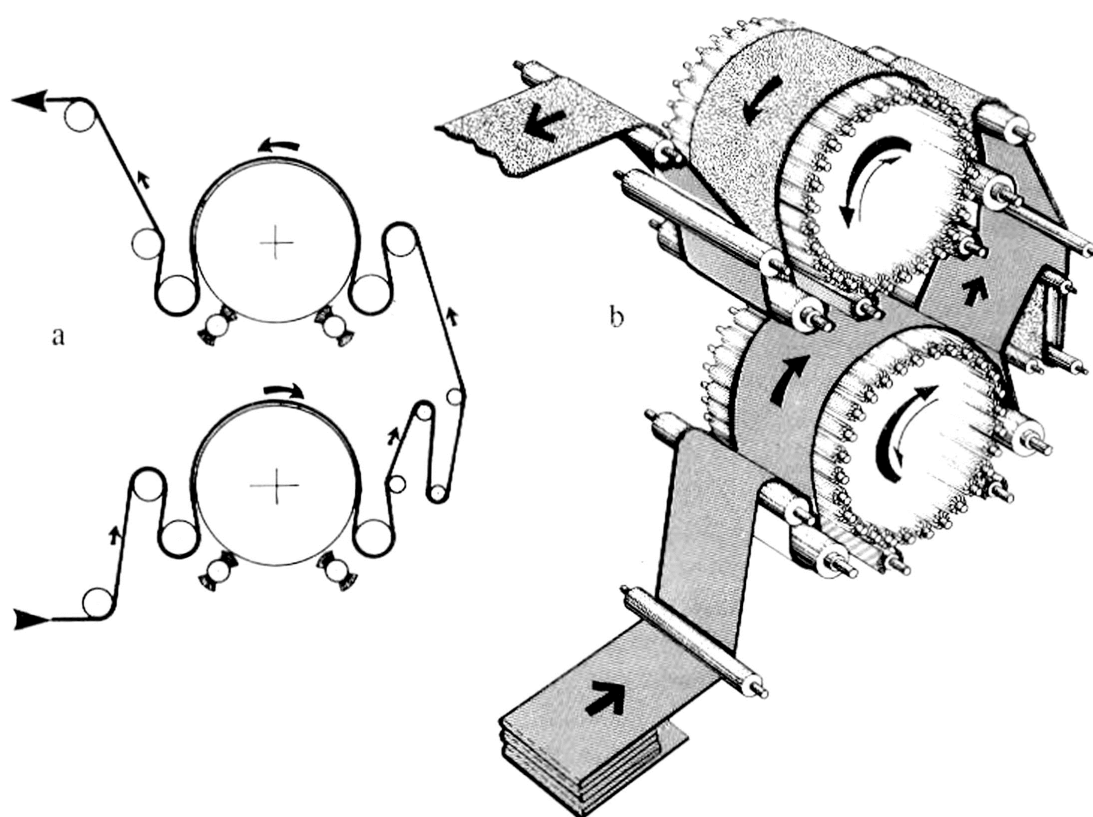
Once a certain limit has been exceeded, the excessive mechanical stress could damage the fabric: it is therefore better, when carrying out a powerful raising, to pass the wet fabric through the raising machine many times (dry when processing cotton fabrics) and treat the fabrics in advance with softening-lubricating agents.

The pile extraction is easier when carried out on single fibres: it is therefore suitable to reduce the friction between the fibres by wetting the material or, in case of cellulose fibres, by previously steaming the fabric.

For the same reasons, it is better to use slightly twisted yarns.

The same machine allows different options of independent motions:

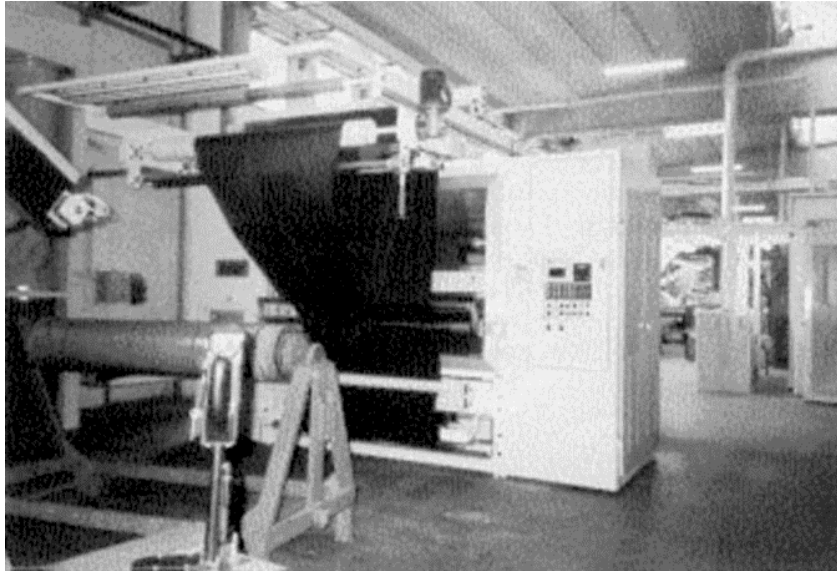
- fabric moving between entry and exit
- motion of large drum
- motion of raising rollers



Picture 124 - Raising the face and back of the fabric: a) scheme; b) view

The raising intensity can be adjusted by suitably combining the above mentioned independent motions, the tension of the textile material, the number of “pilewise” or “counterpile” raising rollers and their relative speed.

It is possible to obtain “combed pile” raising effect, "semi-felting" effect with fibres pulled out and re-entered in the fabric, and “complete felting“ effect.



Picture 125 –Raising machine equipped with 2 rotary drums, each featuring 24 rollers

The raising machine shown in Picture 125 is equipped with two overlapping drums each one featuring 24 rollers, which can process two faces or face and back of the same fabric.

The drums assembled on a standard machine can rotate separately one from the other in the fabric feeding direction or in the opposite direction by carrying out a counter rotation.

In this model all the functions are carefully monitored and controlled by a computer system; in particular all the commands are driven by alternating power motors controlled by "Sensorless" vector inverters. The control electric system features:

- PLC programmable controller for machine and alarms automation;
- touch screen to program and update all processing parameters;
- operating conditions of each single raising process (up to one million "recipes") that can be stored to facilitate the batch reproduction.

Furthermore, a series of special pressure rollers can be assembled on the feeding cylinders to prevent the fabric from sliding, thus granting an extremely smooth raising.

The raising process ability lies merely in raising the desired quantity of fibre ends without excessively reducing the fabric resistance.

For this reason, the technique applying the alternated use of pile and counterpile rollers is the most widely used since it minimises the loss of fibres from the fabric and the consequent resistance reduction.

Standard raising machines have been designed to work with fabrics powerfully tensioned essentially because they are not equipped with an efficient and reliable tension control. This gives rise to the effects detailed below:

- 1) the contact surface between the fabric and the raising cylinders is quite small;
- 2) the hook nibs work only superficially on the fabric and the raising effect is quite reduced;
- 3) the fabric width is drastically reduced.

The above mentioned inconveniences have now been eliminated thanks to the last generation of raising machines (shown in Paris at ITMA 99), which reduce the number of passages and carry out the raising process by gently tensioning the fabric.

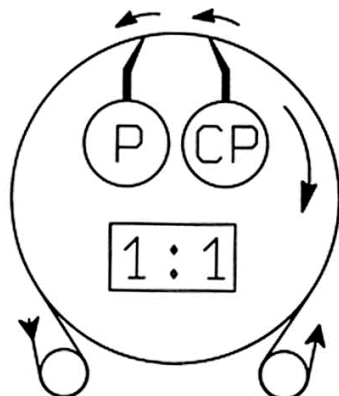
These recent raising machines have been equipped with an extremely accurate and self-adjusting system for feed tension control; the relationships between the ratios of the roller relative speed of the cylinders are electronically controlled by a PLC.

The above mentioned parameters are constantly monitored and adjusted and a wider range of effects can be homogeneously carried out and reproduced; all this results in

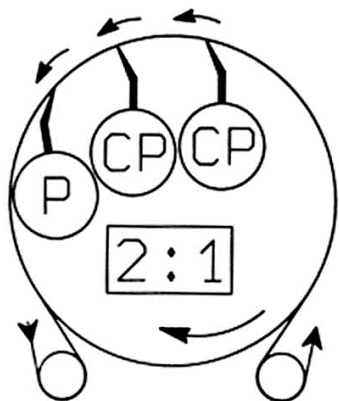
- quality excellency with higher coverage and limited loss of fibres;
- higher production output with a reduced number of passages (up to 50%);
- consequent saving with lower costs per treated fabric unit.

A 24-roller machine can feature one of the following possible architectures :

1:1 Conventional system - 12 CPs + 12 Ps

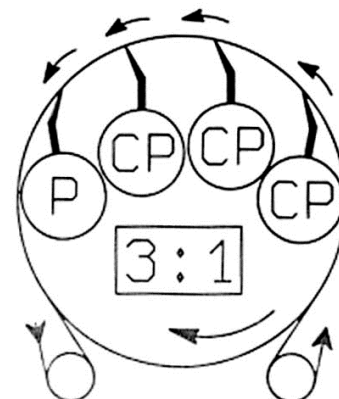


2:1 System - 16 CPs + 8 Ps



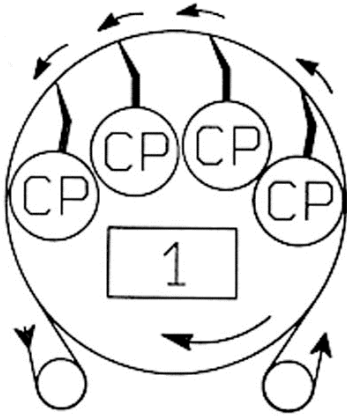
A greater pile density can be obtained with this system since this machine features 4 extra CP rollers (performing as true "raisers"), but the pile length is slightly shorter due to the reduced number of P rollers.

3:1 System - 18 CPs + 6 Ps



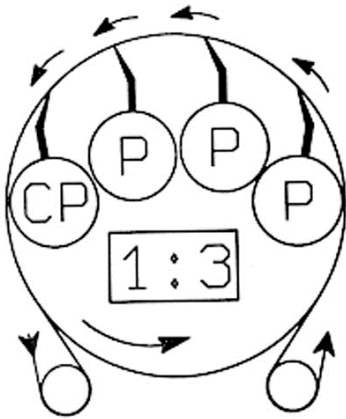
Same as above but now the number of CP cylinders is still greater than 2. Consequently the hair pulled out is thicker but its length is further reduced.

In most cases the shorter piles do not create any problem since the raising process is followed by a shearing (cutting) one.



System 1 – 24 CPs napping unit

This system is used for napping purposes, i.e. to felt the fibre end previously passed on special fabrics such as blankets, cotton plush and/or polyester, polar fleece.



System 1.3 - 6 CPs + 18 Ps

This system is used to loosen the hairs; the number of P rollers is greater than the CP one.

This system is mainly used to loose the hair on polar fleece fabrics before the final shearing process.

Picture 126 – The most common arrangements for a 24-roller raising machine

Wool Glazing Machine

This special machine is used to perform functional finishing on wool fabrics after raising. The machine is made up of two different units.

The **starching unit** includes:

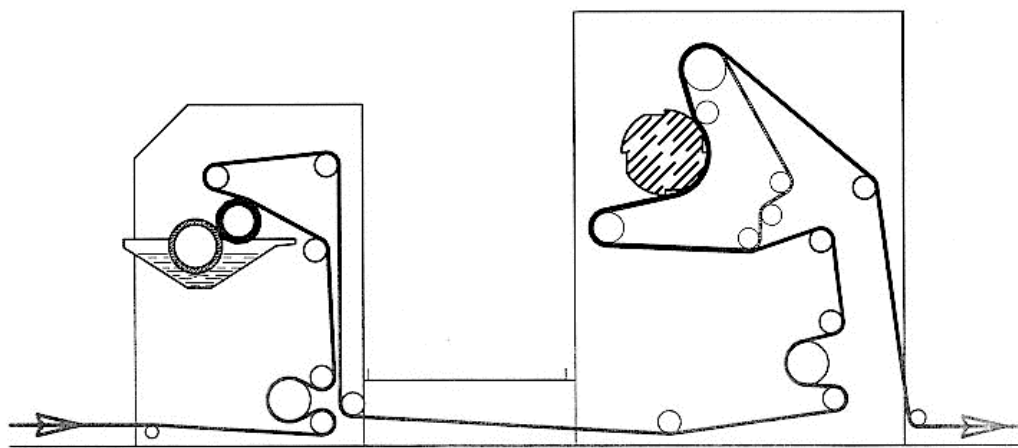
- a vat containing water and silicones;
- a variable-speed extracting cylinder to reduce the quantity of liquid to be passed onto the fabric;
- a brush coated with horsehair adhering to the extracting cylinder and passing the liquid onto the fibre ends of the fabric, simultaneously combing and lining up the fibres.

The **glazing unit** includes:

- a crenellated polishing cylinder (made of steel and coated with hard chrome) heated by means of electric resistances at temperatures up to 220°C and four spiral grooves on which hard-steel combs are assembled. These combs have very fine teeth to enhance the efficiency of fibre ironing during the process;
- a felt sleeve, rotating at the same speed of the fabric, presses the fabric onto the polishing cylinder. The contact arc on the polishing cylinder can vary and the cylinder can reach a temperature of 130°C.

The fabric with the fibre ends already combed and wet come under the polishing cylinder, which dries and irons the pile, and confers a lustrous appearance by giving a soft and smooth hand, also thanks to the silicones added to the starching vat (thanks to this process the fabric acquires a hand similar to the precious wool one).

By adjusting the temperature and the speed of the polishing cylinder, the contact arc of the fabric on the cylinder and the contrasting pressure of the felting material, it is possible to obtain different types of finishing (from the laid down to the perfectly lined up one).



Picture 127 – Wool glazing machine

Shearing

This cutting operation, complementary to raising, determines the height of the fibre end irregularly raised during the raising process; the resulting effect affects the appearance and the hand of the fabric, which becomes velvet-like. The machine is made up of:

- velveting brush
- velveting table
- shearing cylinder equipped with helical blades
- doctor blade
- shearing table
- lubrication felt.

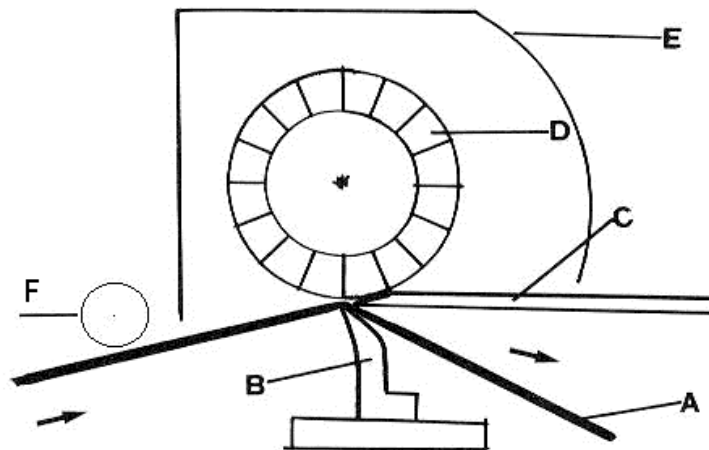
The fabric, after a brushing operation facilitating the raising, is fed on a shearing table forcing it to follow an acute angle direction. In this way the fibres raised by the cutting cylinder are correctly positioned to be sharply cut; the cutting cylinder rotates very quickly and carries out the first blade-cutting operation; the second fixed blade is represented by the doctor blade that stops the pile and cuts it. At this point the action of another brush adjusts uniformly the pile covering the fabric and the suction unit removes the sheared ends.

When the shearing is carried out on velvet fabrics, during the final brushing the pile is not only adjusted but also set by blowing overheated steam on the back of the fabric.

Obviously, to perform a perfectly smooth operation the shearing drum must not oscillate and must show a perfectly circular section.

Also the doctor blade must have a sharp and perfectly even profile and the shearing table must be always positioned at perfectly uniform distance from the doctor blades, with no raised areas.

Depending upon the desired length of the pile, the shearing table, the helical blades and the fixed blade are perfectly adjusted and calibrated: the resulting effects depend upon these adjustments (one tenth of a millimetre accuracy is allowed) and upon the blade grinding.



Picture 128 - A shearing machine: A = fabric; B = gib; C = fixed blade; D = helical blades; E = suction unit; F = brushing drum.

The fabric passes under a rotating brush, which raises the pile and pushes it towards the fixed blade. The fabric is tensioned by means of special gears and slides on a bar provided with a cutting edge that keeps it in a correct position and drives the pile through the two blades. The fibre ends are cut by the contact between the fixed blade and the rotating helical blade; the contact point moves quickly on the whole width of the fabric following the cylinder rotation and cuts the fibre ends between the two blades. Obviously the following cutting passages must be as close as possible to make the weaves on the fabric surface less evident. The

distance of the following cutting passages depends upon the number of blades assembled on the machine (from 16 to 24), upon the cylinder revolutions per minute (from 700 to 1200) and upon the feeding speed of the fabric: $D = V/g n$ (where (V) is the feeding speed of the fabric expressed in cm per minute, (g) is the number of revolutions per minute performed by the cylinder equipped with blades, and (n) is the number of the cylinder blades).

To avoid overheating due to the friction between the helical blades and the fixed blade, a woollen felt (which is usually covered with a special lubricating oil every 2/4 operating hours) is assembled on the cylinder. The shearing units must be controlled and ground at regular intervals. The shearing height is generally adjusted by raising/lowering the shearing unit with reference to the shearing table and only a few hundredths of millimetre accuracy is allowed. These units also include an electropneumatic device, which automatically makes the seam slide under the velveting and shearing unit.

The cuts will be slanting to the fabric. To obtain a better evenness of the fabric surface, the shearing operation must be carried out with two cylinders equipped with helical blades arranged in the opposite direction, or with an even number of passages carried out with cylinders rotating each time in the opposite direction (crosscuts).

Both shearing and raising machines must be equipped with devices which decrease the fabric tension (shearing machines) or raise the blade (raising machines) when the seam joining the cloths passes through the machine; this prevents the fabric from tearing and avoids undesirable machine stops.

Also patterns may be cut into the fabrics by shearing to give a “sculptured effect”, like with raising, or by using special fixed or mobile blades.

Stabilisation

This process produces greater density and stability (e.g. the Sanforset process) and gives the fabric a controlled compression shrinkage, which eliminates distortions originated during previous processes. The fabric finished with this treatment keeps its shape also after repeated washing thus providing an excellent dimensional stability of the textile substrate. The fabric is fed into an opener/tension-adjusting device, and subsequently passes through a wetting unit where the quantity of water necessary for bulking the material is sprayed on the fabric.

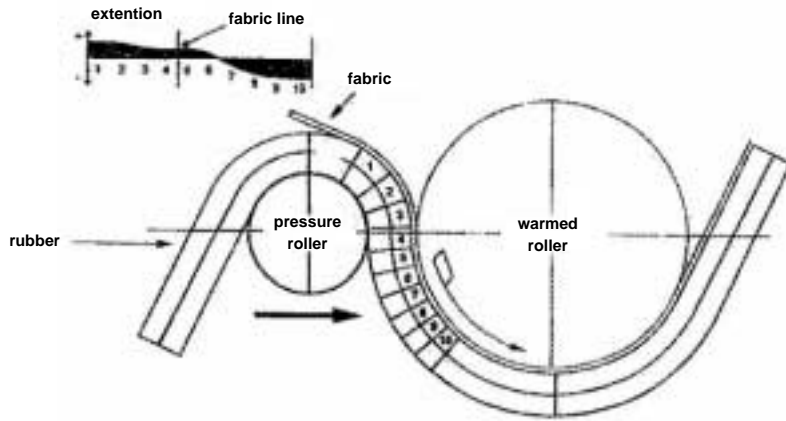
A steaming treatment can be carried out by passing the fabric onto a heated cylinder, which allows the water spreading in the fibre bulk and completes its swelling.

The textile material passes to a stenter which gives the fabric the desired width and is then fed into the rubber-belt squeezing unit.

The fabric shrinkage is carried out with several simple operations: the rubber belt pressed between the squeezing cylinder and the drum is stretched and, once out of this squeezing unit, it again takes its original shape. The fabric is made to adhere to the rubber belt in the squeezing area and, since it can slide more easily on the heated and mirror-polished surface of the drum than on the rubber one, it is forced to follow it during the subsequent shrinkage.

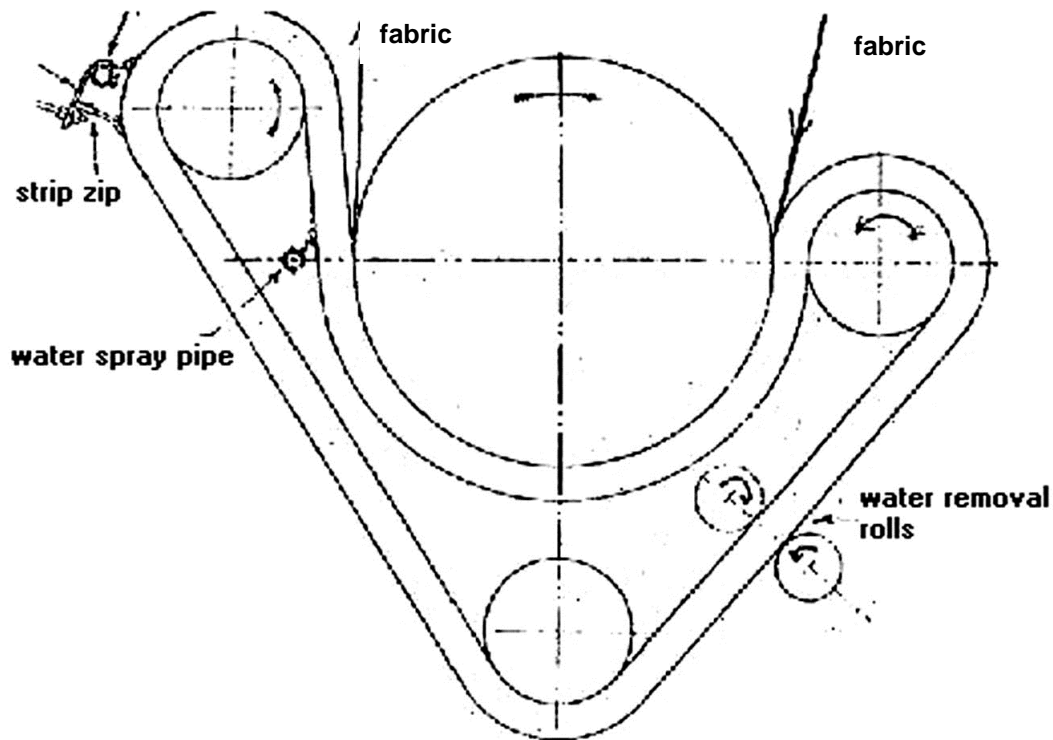
The resulting effect is a continuous and steady sliding between the drum and the rubber belt and consequently between the drum and the fabric. Since the stretching of the rubber belt depends upon the intensity of the pressure exerted by the squeezing cylinder, each pressure variation corresponds to a shrinkage variation.

Therefore the higher the pressure the greater the shrinking effect.



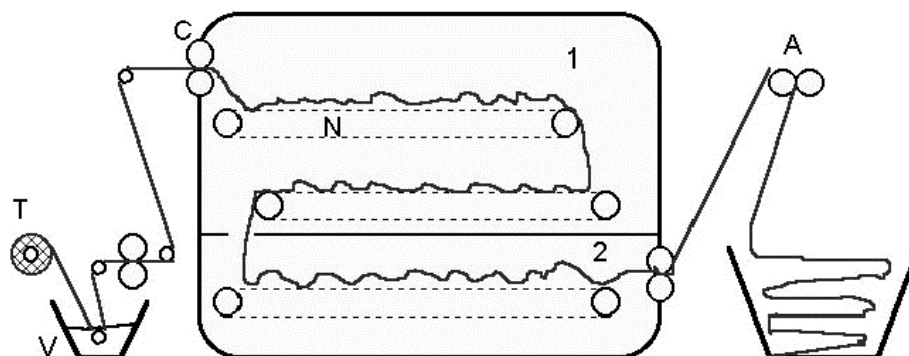
Picture 129 - Compacting process

After leaving the squeezing unit the fabric is sent out to the drying unit (180°-190°) with the slightest possible tension. The fabric is fed into a felt calender, which sets the shrinkage. The fabric immediately after the squeezing compression must be subjected to the slightest tensions and the moisture must not exceed optimum values.



Picture 130 - Shrink area

Tubular knitted goods can be treated on stenters (to impart dimensional stability), only after the cutting operation and eventual bonding. Drying and dimensional stabilisation of tubular knitted goods can be obtained by passing the relaxed fabric into belt drying units and by steaming them in the final path.



Picture 131 – Compacting process for tubular knitted fabrics

The fabric (T), wet or dampened with a solution containing softening agents in a vat (V), is laid down, overfed by a little calender (C), on metal-mesh vibrating conveyor belts (N) into a drying unit. On the first two conveyor belts, the fabric is dried with hot air (1) while vibrations make the fabric shrink freely; the steaming treatment (2), which sets the dimensional stability, increases the fabric bulk and gives a soft hand to the fabric, is carried out on a third conveyor belt. The fabric is then folded in a special folding unit (A). In case of further cutting and bonding units, a shrinking machine can be added to the system.

Decating

This process is mainly carried out on wool by exploiting its elastic properties in hot and wet conditions by the direct action of the steam on the fabric. This treatment gives the processed fabric the following characteristics:

- 1) dimensional stability;
- 2) setting of pile after raising;
- 3) reduction of possible glazing effect after calendering, thank to the swelling caused by steam blown on fibres;
- 4) modification of the hand, which is much more consistent after the treatment;
- 5) pre-stabilisation to autoclave dyeing

This category of treatments does not include the stabilisation of wool fabrics such as potting, where the dimensional stabilisation is obtained thanks to the "plasticisation" phenomenon occurring when the wool fabric is immersed in hot water.

On fabrics made with other fibres, the same treatment can be carried out as "steam ironing" alternatively to the calendering treatment, when an excessive "glazing effect" could result from the treatment.

The steam decating, which is also referred to as dry decating, is carried out on decating machines in one continuous treatment or two discontinuous ones, according to the following operating techniques:

- drum decating (alternated at atmospheric pressure);
- autoclave vacuum decating (KD);
- continuous decating.

Alternated decating.

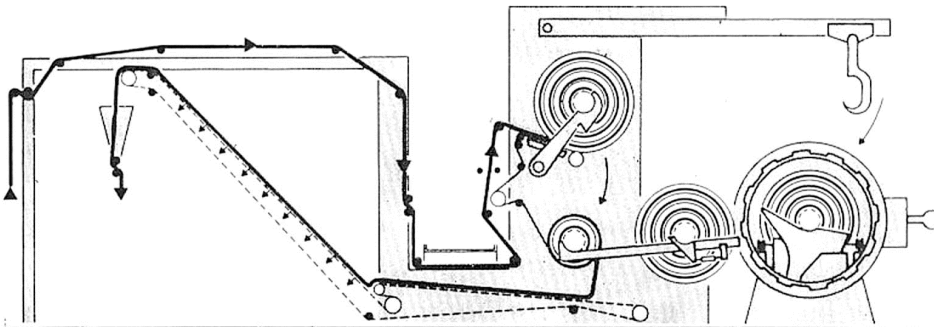
In discontinuous decating processes, the fabric is wound, together with the “satin” (2) or “beaverteen” blanket (1) – on a large perforated drum (90 cm) on which some meters of blanket or similar cloth have been previously rolled.

By using large rollers, it is possible to wind the same quantity of cloth with a thinner density of the roller, to allow the steam imparting a more uniform effect and reducing the differences between the tail and the head.

The steam, at a temperature that can reach 130°C and a pressure of up to 6 bars, is forced into the cylinder through the fabric roll (i.e. it is forced through both fabric and blanket) for an interval of time that can range from 1 and 3-4 minutes, according to the desired effect. The steam is then exhausted by means of a pump.

Autoclave decating (Kessel-Dekatur)

Thanks to the possibility of reaching higher temperatures (130°C) and greater pressures (up to 6 bar), the setting effect is markedly more durable than when working at atmospheric pressure. This treatment is now well appreciated and commonly used to give dimensional stability to all combed fabrics and also to some carded ones. The machine can be divided into two main compartments: the fabric taking up area and the horizontal autoclave. Recently, semi-automatic systems have been successfully developed and improved thanks multiple-position stations, which allow preparing a new roller and unloading the treated one while a third roller is undergoing the decating treatment.



Picture 132 – Loading system of a pressure decating unit

(1) *Beaverteen*: raised technical fabric, used as a blanket in fabric decating process when the desired effect is a bulky hand and a matt appearance.

Technical features of the most common types of beaver teens: width ranging from 176 to 178cm, weight varying from 190 to 600 gr/m²; thickness 1.5-2mm; structure: polyester warp, cotton weft; polyamide warp, cotton weft; warp and weft 50% polyester/50% cotton.

(2) *Satin*: technical textile used as a blanket in discontinuous decating (in drum or autoclave).

The main characteristics of a “satin” are the following:

- 1) dimensional stability;
- 2) consistent steam permeability;
- 3) resistance to chemical agents and to steam;
- 4) no negative side effects.

The most common fibre structures are the following:

- 1) polyester (65-50%)/cotton (35-50%), weft and warp;
- 2) 65% polyester warp / 35% cotton; 65% cotton warp/ 35% polyamide;
- 3) warp and weft 65% cotton / 35% polyamide.

The life of a “satin” depends upon:

- 1) the presence of chemical products on the fabric;
- 2) the quality of the steam.

It is worth considering that the setting effect is directly proportional to the increase of process time and steam pressure and consequently to temperature. The increase of both factors causes a marked yellowing of the wool together with a progressive deterioration of the peculiar qualities of the fibre (resistance, elasticity and soft hand).

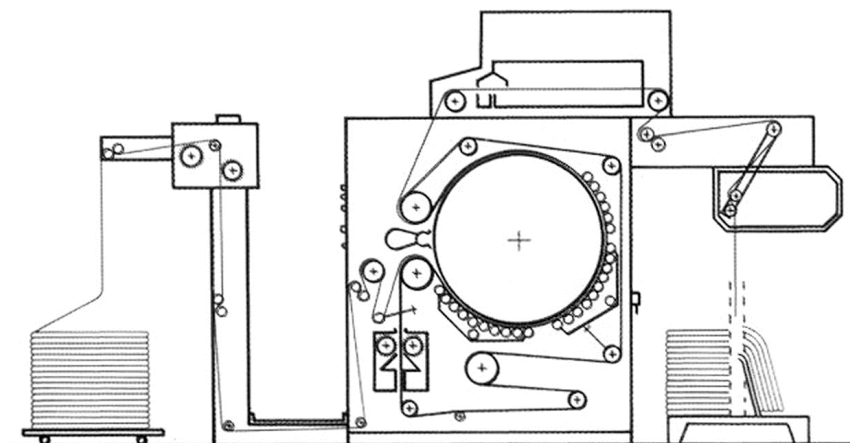
Continuous decatizing

The need to speed up the processing cycles has led to the development of continuous systems, which give better output rates, no head-tails differences, no marks on the fabrics due to seams necessary to sew the heads and sometimes moiré effects (surface pattern resembling water ripples). The only disadvantage is a less powerful effect given by the treatment; in particular an unsuitable stabilisation for all products.

The continuous decatizing process carried out under pressure allows a permanent setting of the wool fabric, which is obtained through a first processing step with saturated vapour under pressure (which can reach a temperature exceeding 135°C), while a second cooling step grants the surface and dimensional stabilisation.

For handling purposes, the fabric is compressed between a large perforated roller, coated with a heavy textile coat and a thick endless layer made of dense cotton/polyester felting material.

All along its path the fabric is treated (using different systems) with steam supplied by means of special delivering units assembled under the conveyor belt in the lower part of the cylinder, and subsequently cooled with air. The intensity of the treatment can be adjusted by adjusting the process speed, the pressure between the cylinder and the conveyor belt, the moisture degree and the steam pressure.



Picture 133 - Continuous pressure decatizing process

Steaming

The tensionless steaming process of wool fabrics is the most widely used technique to obtain a good dimensional stability to ironing with steam press.

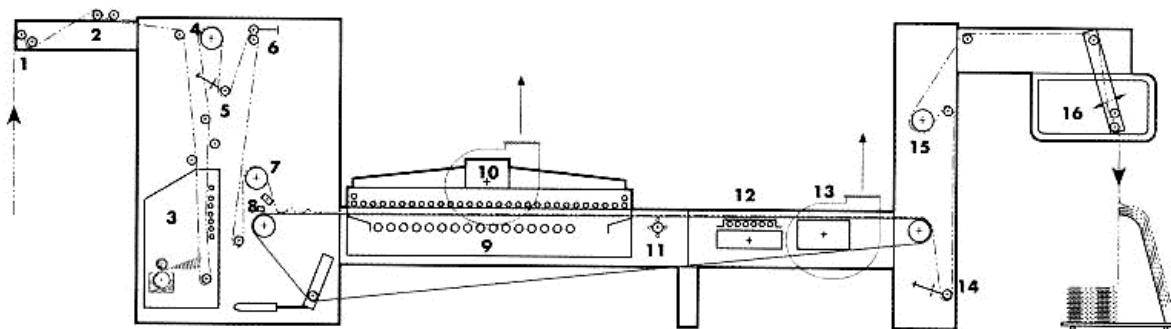
The steam action involves the hygroscopic swelling of the fibres with a subsequent relaxation or shrinkage of the fabric, which recovers its "natural" shape.

The steaming process eliminates also all the residual tensions. The machines used to carry out this treatment are called tensionless steaming machines (tensionless steaming) or steaming-shrinking machines.

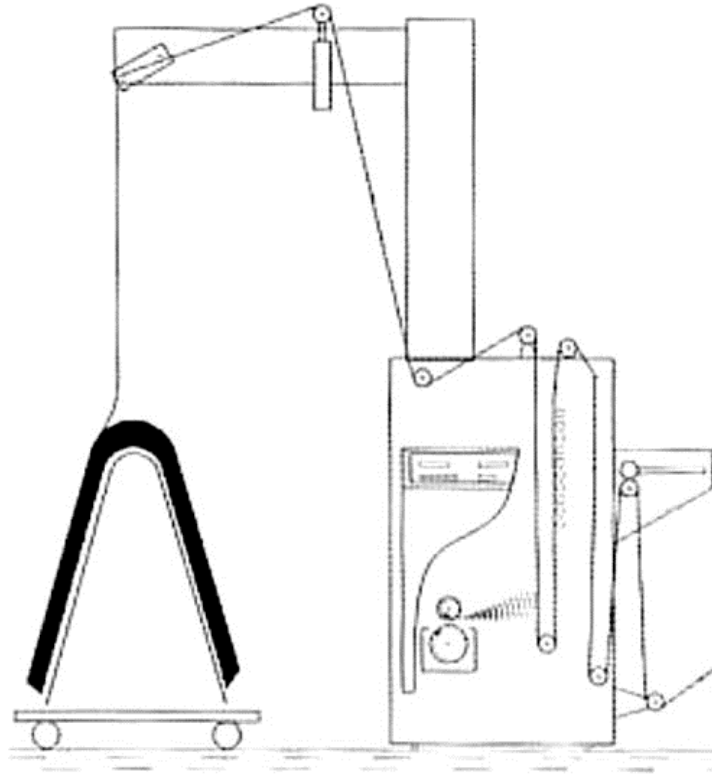
The tensionless steaming units can be divided into four main sections:

- 1) feeding section where the fabric is laid on a continuous conveyor belt by means of an overfeeding system coated with a technical fabric made of synthetic material, stable in regard to the action of heat, featuring such a weave to ease passage of steam. It generally vibrates for a better relaxation of the fabric and keeps it quite suspended inside the steaming tunnel.
- 2) steaming area with one or two steaming tunnels with a suction system.
- 3) cooling area equipped with a suction unit assembled under the conveyor belt to eliminate the residual moisture.
- 4) fabric take up area, where a dandy roller or an optical control system adjust the speed to prevent any stretching of the rolled or folded fabric.

Technical innovations applied to the steaming processes aim at obtaining a better and final relaxation of the fabric and a reduction of the steaming stage, which requires a great quantity of steam (which is mostly dispersed outside through vents) and long processing times, since good results can be obtained only by keeping the fabric in contact with steam for a long time. The various machine manufactures have developed special systems to cut processing times and steam quantity and obtain an optimum relaxation of the fabric. The system shown in Picture 134, features a programmed and controlled dampening system assembled before the steaming tunnel.



Picture 134 - Steaming-shrinking unit: 1) double braking bar; 2) fabric centring device; 3) dampener; 4) adjusting cylinder; 5) compensating cylinder; 6) moisture sensor; 7) feeding cylinder; 8) feeding sensor; 9) steam application field; 10) suction hood; 11) vibrating device; 12) blowing unit; 13) suction unit; 14) fabric unloading regulator; 15) fabric unloading cylinder; 16) variable folding device.



Picture 135 - Detail of the automatic fabric dampening system

The dampening system has been introduced into the steaming unit for the reasons detailed below.

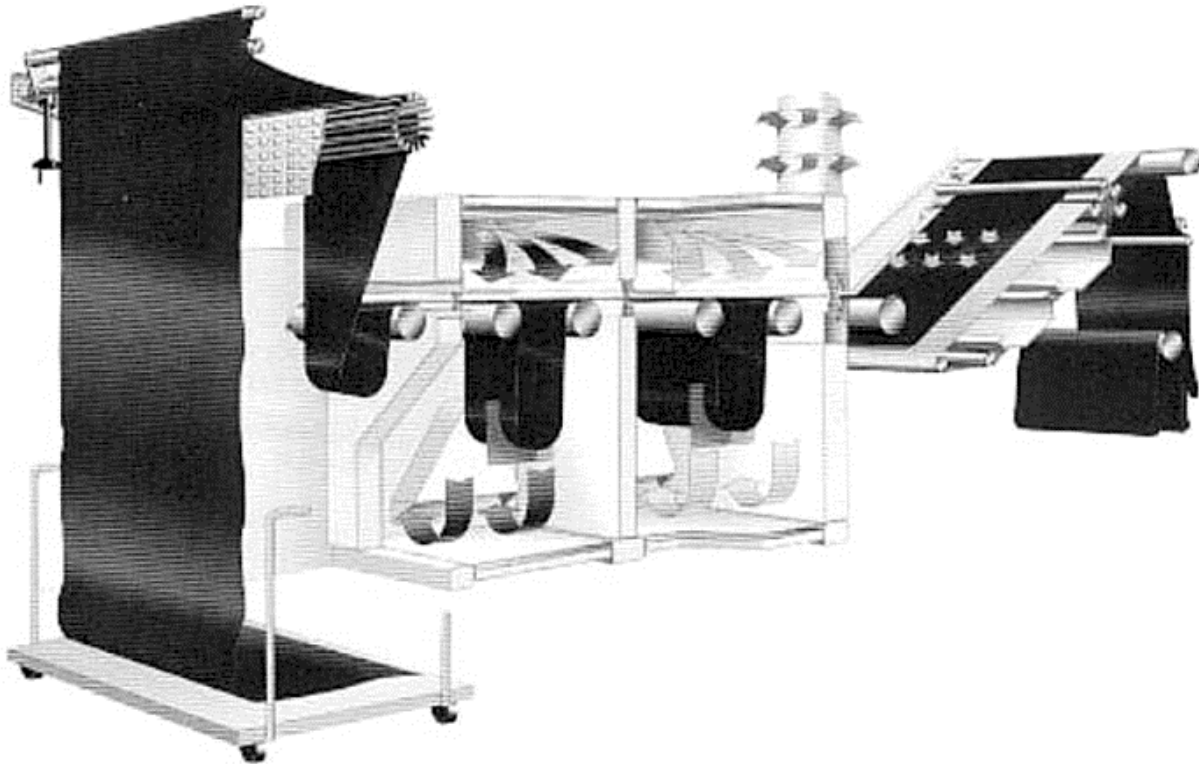
- Steaming generally tends to reduce the moisture percentage dispersed in the fabric and therefore the pre-dampening operation grants a recovery ratio of the fabric after the treatment certainly better than the one obtained with a standard system.
- The moisture dispersed in the dampened fabric fed into the steaming system is transformed into steam thus providing better shrinkage and relaxation results.
- Commercial tests have shown a remarkable steam saving obtained thanks to the vaporisation of water previously sprayed on the fabric.

The set up of the steaming-shrinking-crabbing unit has allowed great steam saving, a remarkably increased output rate and high-quality final results.

The basic elements characterising this new type of steaming unit are detailed below:

- the steaming tunnel with new design and architecture, grants an efficient air exhaust and the addition of a saturated vapour compartment with almost no-oxygen prevents any possible fabric defect caused by standard steam feeding units;
- the steam is fed and controlled according to the real consumption, thus avoiding any dispersion inside the tunnel;
- the temperature is controlled and adjusted according to the type of fabric and fibre to be treated;
- any outlet exhausting in the atmosphere has been eliminated and consequently all heat dispersion has been eliminated.

In another type of steaming machine the fabric is exposed to the steam action with tensionless feeding thanks to a suspended fabric system which avoids the use of a conveyor belt.



Picture 136 – Shrinking-steaming machine with hanging fabric

The suspended fabric system has the following advantages:

- energy saving with the same relaxation effect thanks to the steam recirculated into the steaming compartments;
- lower processing temperatures, greater quantity of water vapour;
- longer dampening times with the same machine speed, due to a greater quantity of fabric fed into the "hanging fabric compartments ";
- automatic self-adjustment of the tensionless take-up of the fabric inside the compartments, thanks to the shrinkage controlling system which monitors each single cloth and to the improved driving system.

The system includes a double cooling compartment with forced ventilation (thermal shock) in the final section aiming at simultaneously cooling down the fabric and relaxing the internal tensions of the fabric structure.

Chemical Finishing Treatments

By applying chemicals of different origins, a fabric can receive properties otherwise impossible to obtain with mechanical means.

Chemical finishing treatments:

- allow the stabilisation of fabrics already subjected to mechanical finishing processes, such as calendering;
- give fabrics some properties (e.g. flame retardancy and water repellency), which would be otherwise absent

The products used can be classified as follows:

- **Natural** (adhesives, fats, oils, starches)
- **Artificial** (modified starches, modified cellulose)
- **Synthetic** (synthesis products) including: N-methylol derivatives (thermosetting, reactants), linear reactants (carbarnates, epoxy resins), thermoplastic polymers (vinyl, acrylic, polyethylene), polyurethanes and silicones.

This classification, helpful for students, does not coincide with the products actually sold on the market since these products are blends containing also catalysts and auxiliaries which interact and produce complementary effects. It is therefore necessary to underline how chemical finishing can affect the textile product by altering its mechanical properties, sometimes changing the colour shade or its original colour fastness.

Different techniques are available for applying the above mentioned finishing substances: by solution, dispersion, and emulsion, pad wetting, exhaustion, coating, spraying, etc.

The most appropriate technique must be carefully studied for each fibre type, and the most suitable chemical finishing process applied to obtain optimum results and grant a reasonable safety margin for any possible error.

Application of the finish

The operations to be carried out when applying the finish to a textile substrate are mostly conditioned by the structural and hygroscopic properties of the material to be processed, by the desired effects, by the physical and chemical nature of the elements that make up the finishing substance and by the machine's output rate. In textile finishing, we can distinguish between five main application techniques:

- a) padding;
- b) spraying by means of atomisers;
- c) exhaust process in treatment liquor;
- d) coating carried out by means of doctor knives;
- e) controlled application of low liquor quantities.

Padding is by far the most common among the various finishing techniques.

Padding

This is certainly the most popular process for both the most conventional and innovative finishing treatments. The machine used for this process can be referred to with various definitions such as padding unit, squeezing unit, etc. After ensuring that the textile substrate can be padded by evaluating its mechanical and structural properties, this technique can be applied to carry out all wet finishing operations, except for some cases (see pad dyeing for details about the machinery used).

Spraying

The application of finishing substances by spraying is used for carrying out gentle finishing processes which leave on the textile material a small concentration of products, and is particularly indicated for applying softening, anti-static and anti-mildew agents. For a good and homogeneous penetration and diffusion of the finish in the textile material, it is better to let the sprayed and wound fabric rest for some hours before drying.

In the last few years, a very important field has been developed in the textile sector, i.e. the production of webs made of synthetic fibres. For this particular type of product, the resin-coating process is carried out only by spraying the finish directly on the fibrous substrate and by generally applying synthetic resins in aqueous emulsion.

Exhaustion

The treatment of yarns or fabrics in exhaustion liquor is recommended above all when stable chemical products are applied on the textile substrate.

The manufacturing process undergone by the material is useful to precisely evaluate the best method for applying the finish, for example on hosiery or tubular knitted goods. From a chemical point of view, the most suitable products for the exhaust process are those with cation-active properties. In particular cation-active softening agents are often applied with this process, as well as paraffin- and wax-based emulsions, and more recently, cation-active polymer emulsions.

Coating

At present, after the launch and diffusion of synthetic resins, the so called "coating and bonding" applications have been experiencing an extraordinary growth, above all in Italy.

Coated and bonded fabrics are now simply classified, according to their end use, i.e. for garments, upholstery, draperies and tapestries, footwear, leather goods and technical articles.

Generally the process starts from a fabric or from a non-woven fabric as a "backing".

All fibres can be used, from light silk to linen and hemp, from synthetic fibres to glass fibres.

As regards the resins used for the coating layer, manufacturers once employed only natural substances, but are now using almost exclusively synthetic polymers of high molecular weight.

Today manufacturers are constantly in the search for coating substances that are more and more elastic, able to withstand different mechanical stress and washing conditions, and above all resistant to wearing and weather agents.

These coating polymers are bonded to the fabric backing by means of calenders, in the form of thin sheets or are mainly spread in the form of aqueous dispersions or solutions in solvents.

The characteristics and the properties of coated fabrics depend on the chemical structure of the coating resins applied and the type of backing fabric used.

The coating layer undoubtedly plays the most important role for appearance, hand and resistance properties: its elasticity, its behaviour at high and low temperatures, its resistance to abrasion, to solvents and to the effect of ageing and weather agents, depend on its chemical composition as a substance with a high molecular weight and more or less thermoplastic qualities.

The coating technique

Coated fabrics are divided into specific categories according to the following scheme:

- fabric based on natural, artificial and synthetic fibres;
- coating layer of natural or synthetic resins.

The coating layer can be obtained with the following processes:

1. bonding with thin resin film;
2. direct coating with resins;
3. indirect resin coating with the transfer technique.

In the first process method, now scarcely used, the fabric is bonded to its fabric backing on special calenders.

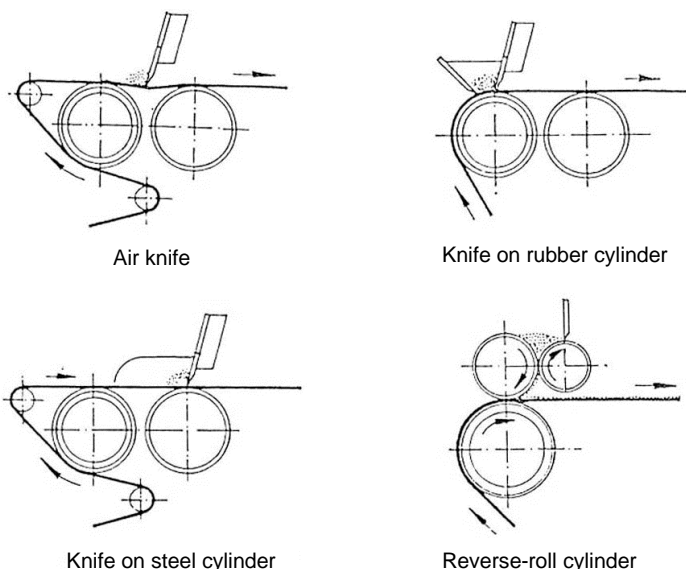
This process is still used today to manufacture tablecloths by applying a thin PVC film to the fabric.

In the direct coating process the resin is spread directly on the fabric by means of a doctor knife or a cylinder with the following methods:

- air knife;
- knife on belt;
- knife on cylinder;
- "reverse-roll" cylinder.

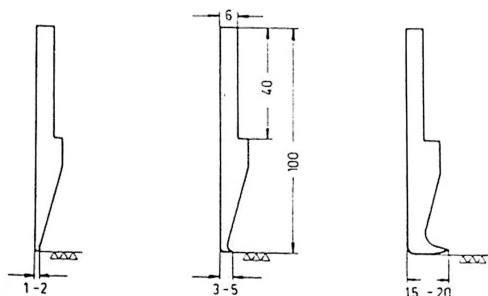
Since the fabric, in all the above mentioned cases during the coating, drying and winding operations is always subject to warp wise tension, these coating methods can be only used on compact or stretch-resistant fabrics.

Obviously these methods cannot be used on knitted goods. During the air coating process and the belt coating one, the quantity of resin spread is relatively small and the desired thickness can be achieved only by applying successive layers, each one stabilised with an intermediate drying stage.



Picture 137 - Doctor knife coating

The knife can have a more or less rounded profile; the quantity of resin spread is measured in grams per square meter of dry substance and is determined by the dry content of resin, by the coating speed and by the knife profile.



The greater the process speed, the smaller the quantity of resin spread; the sharper the knife, the smaller the quantity of resin spread on the fabric. This coating method is used to produce waterproof fabrics for rainproof textiles, umbrellas, tapestries and technical items. The most commonly used resins are the acrylic resins in solvent or aqueous dispersion and single or bi-component polyurethane resins.

Picture 138 – Blades for doctor-knife coating

With the reverse-roll cylinder method it is possible, within certain limits, to apply a thick coating layer, i.e. greater quantities of resin to fill a specific gap. In cylinder coating, the doctor knife usually has a finger's nail profile and the quantity of resin spread is measured in grams per square meter of dry substance or in hundredths of millimetres of coating layer thickness.

A direct coating unit consists of a series of coating heads alternated with drying ovens or tunnels, each one with cooling cylinders at the exit. The drying temperatures depend on the type of resin used, whereas the coating speed is determined by the length of the drying ovens, the air exchange, the coating system and the rheological properties of the resins applied: the reverse-roll method allows very high coating rates up to 70 m/min compared to the 15 to 18 m/min of other methods. The reverse-roll method is applied to the following goods:

- rainproof textiles;
- waterproof canvas;
- coated fabrics for leather goods and cases;
- coated fabrics for garment and upholstery;
- reverse coated fabrics for wall coverings;
- coated fabrics for footwear.

In the indirect coating technique, the coating material is first spread on a special paper (the so-called release paper) and is then transferred onto the backing fabric. The coating layer consists of a layer of resin spread directly on the paper and of a second layer of resin, which acts as bonding agent between the first layer and the backing. The backing can be of different materials with different properties. The release paper, which must be compatible with the resin applied, can be glossy, matt, smooth or embossed.

The steps to be carried out in an indirect coating process are the following:

- application of the first resin layer on the release paper (1st coating head);
- drying (1st oven);
- cooling;
- application of the second resin layer (adhesive, 2nd coating head);
- bonding to the backing (woven or knitted fabric, etc.);
- drying (2nd oven);
- removal of the coated fabric from the paper and fabric winding up;
- paper winding up.

The paper coating step is carried out using a cylinder and “finger’s nail” knife. The coating speed is relatively low and varies according to the resins to be applied; it can range from 4 to 20 m/min.

With this coating technique it is possible to manufacture a number of different articles of different appearance and hand. The appearance of the coated surface depends on the type of paper used (glossy, matt, smooth or embossed), while the ultimate hand properties are determined by the resin quality and quantity, the adhesive agent applied, the backing fabric and its preparation.

Here are some substrates that can be processed with the indirect coating technique:

- imitation leather for upholstery and garments;
- imitation leather for footwear;
- imitation leather goods.

Controlled application of small liquor quantities

Water is the most common medium used for applying the finish, and must be subsequently removed from the textile material after the treatment. A drying process is quite expensive. Therefore, to avoid additional costs, new techniques have been developed that allow a controlled application of limited quantities of the finish liquor. In fact, most of the water on the fabric surface or between the fibres can be eliminated with mechanical hydroextraction processes (centrifuge, suction, squeezing, etc.) but these processes will hardly remove the moisture dispersed in the capillary spaces inside and between the fibres.

In hydrophilic fibres (for example cotton), the limit of residual water that cannot be eliminated by means of a mechanical process ranges from 40% to 50%.

To obtain a homogeneous distribution of the finish in the fabric it is (theoretically) necessary and sufficient to only saturate the capillary areas of the fibres.

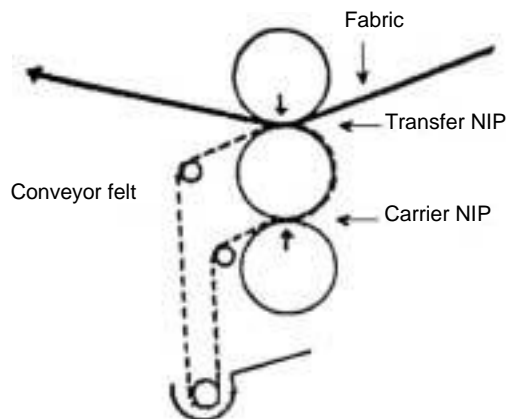
The quantity of solution corresponding to the water necessary for a complete swelling of the amorphous areas of the fibres is called "Critical Add on Value" (CAV) and is determined by the fibre nature and by the fabric structure.

Following the application of greater quantities of solution, during the drying process unstable finishing products can migrate towards the surface of the fabric, thus leading to inconsistent distribution of the finish on the substrate (internal yarn areas are poorer of finish.).

On the contrary, for an optimum application from both a technical (penetration and uniformity) and a cost-efficiency point of view (minimum energy consumption for drying), it is necessary to apply a quantity of solution equal to – or slightly exceeding – the CAV.

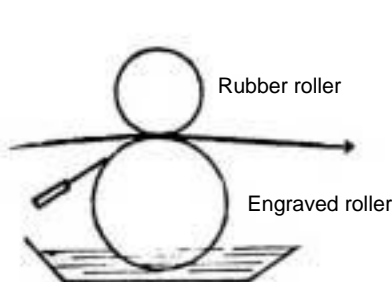
For cotton, this means that only 30-35% of the liquor needs to be applied. The various techniques are briefly described below.

1. Liquor transfer: a continuous felt is impregnated with the finishing solution and then squeezed between two rollers with a pick up rate of about 70%. The fabric to be treated is made adhere against the felt in a second squeezing unit. The squeezing pressure transfers to the fabric about half the liquor in the felt. By controlling the pressures in the two squeezing points separately, the quantity of liquor applied to the textile material can be accurately controlled and the variations per square meter of the fabric (within a certain range) can be evaluated with precision.

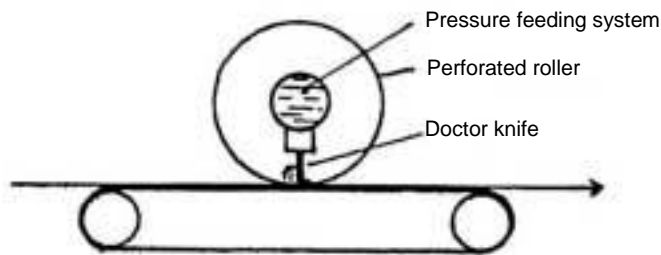


Picture 139 - Padding unit

2. Finish printing: a finely engraved roller is partially immersed in the finishing liquor. The liquid in excess is removed by means of a doctor knife.



Picture 140 - Finish printing



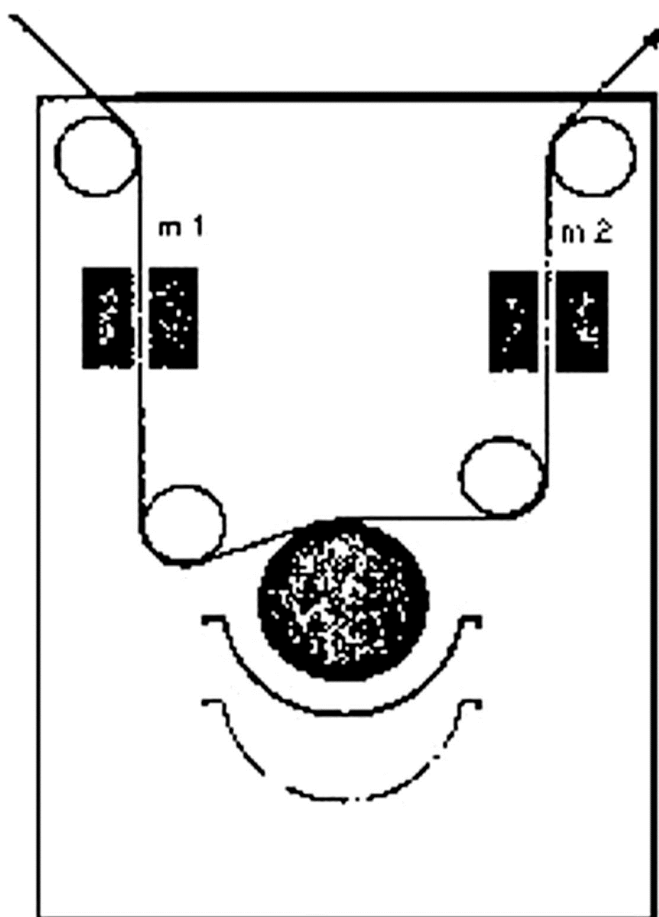
Picture 141 - Foam systems

The liquor remaining in the engraved roller is then transferred to the fabric by means of the pressure exerted by a second roller. By using special gluey finishing solutions, it is even possible to perform printing processes with hollow rollers. (See hollow-rollers printing.)

3. Finish foaming: small quantities of water can be left on the fabric by applying controlled quantities of foam. Foam is in fact made up of 5-10% aqueous substance and about 90-95% air. Foam is generated with special devices by blowing compressed gas (usually air) in the solution containing a surfactant. The viscosity degree of the solution and gas are so adjusted to obtain air bubbles of roughly uniform diameter (50-100 μm) forming a stable and creamy foam. The foam is then deposited on the fabric in layers by means of a doctor knife. The foam, after being applied, must be settled so that the fabric can absorb the padding solution.

4. Semi-immersion systems: a finish application roller partially immersed in a finishing liquor, rotates and touches the fabric at proper speed to obtain the application of the desired quantity of solution.

This application can be controlled and optimum results can be achieved only when a precise ratio is established between the speed of the application roller and the speed of the fabric. Since the fabric speed can be modified within a wide range (it can be controlled, for example by means of moisture sensors assembled at the exit side of the drying unit), the speed of the application roller must be controlled by special devices that measure the quantity of applied liquor. These measuring devices evaluate the β radiation (generated by krypton 85) absorbed by the wet fabric. One of these measuring devices (m1) is placed before the contact point of the fabric with the application roller, while a second one (m2) measures the quantity of β radiation after the application of the finishing product.



Picture 142 – An immersion system

The difference of signal between the two instruments is kept at a value corresponding to the application of the desired liquor quantity: in fact, each variation of this value determines a variation in the speed of the application roller, in order to bring the quantity of applied solution to the optimum value. For a smooth application on the fabric, a homogeneous liquid film must be created on the roller surface. This can be obtained with a special surface of the roller, but also by using the correct finishing products and auxiliaries (for example non-foaming agents.)

Softening

As a general rule, each fibre has its specific softness value, which depends on its chemical composition and physical structure (less crystallinity = greater softness). The fineness of the fibre or of the filament directly affects the softness of the yarn (woollens, worsteds, microfibres etc.). The yarn twist ratio is inversely proportional to its softness.

The weave also contributes to reducing (closer weave = cloth) or increasing (looser weave = satin) the fabric softness. Furthermore, a greater number of yarns per centimetre increase the stiffness of the fabric, thus reducing its softness.

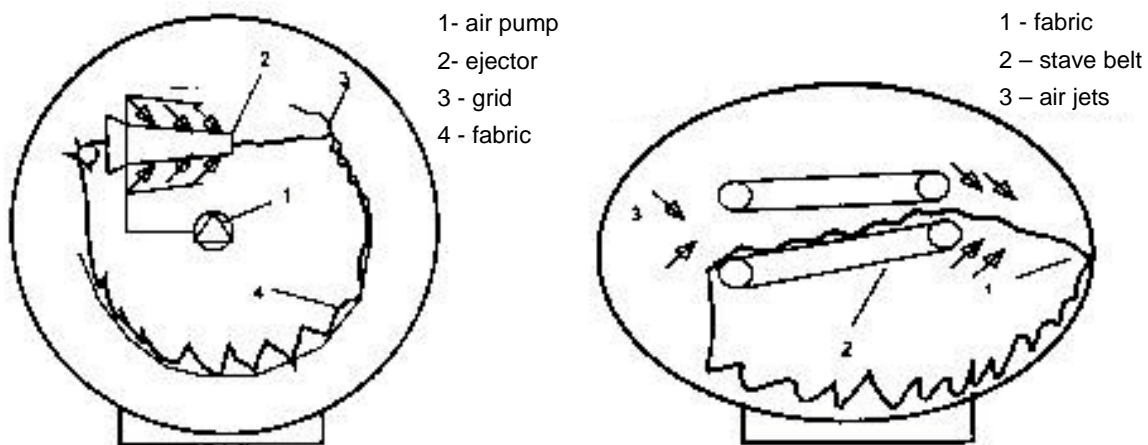
Softening is carried out when the softness characteristics of a certain fabric must be improved, always carefully considering the composition and properties of the substrate.

It is also worth underlining that no standard methods have been developed and established to determine exactly what the softness of a fabric is. This evaluation is therefore almost personal and carried out on the basis of operator's experience. It is anyway possible to distinguish between many types of softness:

- a) surface softness,
- b) surface smoothness,
- c) elasticity (to compression and stretching).

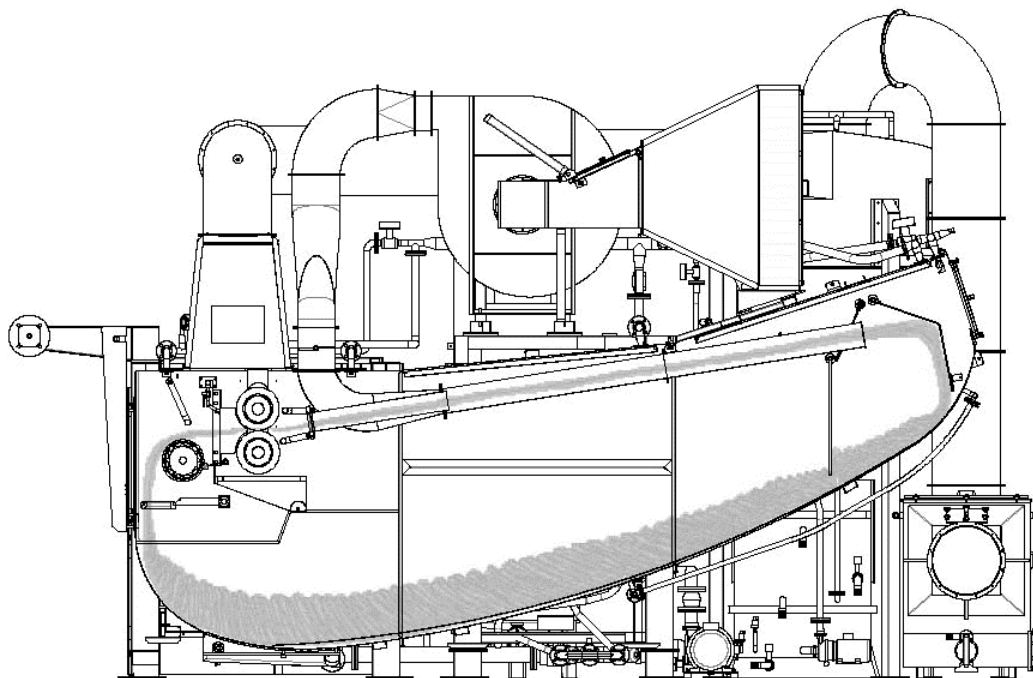
To change the hand properties of a fabric, we can apply mechanical, physical, chemical or combined techniques; some of these methods (sueding, raising) have already been explained in detail in previous sections of this handbook, while some others refers to machines that give different degrees of softness, by means of high-speed rope processing in wet or dry conditions, with the drying stage carried out during the treatment (with or without softeners or enzymes.)

The functional core of these machines are the two tunnels where the fabric is fed through two Venturi tubes. The energy applied for drawing the material is produced only by air and pressure. The fabric flowing through the Venturi tubes is pushed at high speed against a grid on the machine rear side; the fabric then slides on Teflon-coated chutes and reaches the machine front side to start the cycle again; the fabric can reach a speed of 1000 m/min., depending on the type and weight of the different textiles to be processed and according to the desired results.



Picture 143-144 - Schemes of fabric softening machines

The following picture details an industrial softening system.



Picture 145 – A fabric softening machine

This unit applies physical and mechanical principles on fundamental elements such as:

- air, which is the fabric propeller and drawing element;
- the mechanical stress exerted on the fabric inside the Venturi tubes and the stress due to the impact against the rear grid;
- the eventual action of heat.

It is also worth noticing that water is not a crucial element for the process; it is only a medium for carrying dissolved non biodegradable chemical additives (if required.)

The combination of all these elements, almost free of polluting charge, cause the structural modification of the fibres making up the fabric.

They result in more or less marked surface modifications, which can radically change the appearance and the sensorial properties of the fabrics.

The complexity of the finishing action starts inside the Venturi tube where the tail of the fabric is subjected simultaneously to a compressive action and to a subsequent series of vibrating pulses which tend to "random-modify" and compact the textile structures, eventually giving them different properties.

The one-way thrusting force is transformed into a impact force against the grid on which the fabric is pushed when emerging from the Venturi tube; this causes other modifications of the fabric and add structural and surface effects.

This simple treatment that combines physical and mechanical principles, carried out at a precise temperature set by the operator, is sufficient to create particular effects on the morphology of fibres and the weave.

The modifications produced by this treatment are very different and not only affect the colour, appearance and hand properties of the fabric, but also add new properties, e.g. modifying the refraction and diffraction of light on the fabric surface.

The most notable effects in terms of style and added value are obtained on linen, a precious delicate fibre, particularly difficult to process without using chemicals.

The combination of a chemical product or an enzyme liquor with the mechanical treatment can be carried out not only on linen but also on many other widely used fibres such as Tencel and polynosic fibres, imparting a draping, full and lively hand.

All these effects are obtained thanks to the air thrust and to the following impact against the grid, or to the pressure of rollers on the fabric rope.

Comparing the effects of this treatment on a Tencel fabric and on a similar treatment carried out on a dyeing machine, we can see that, as previously explained, this finishing process not only affects the appearance of the fabric, but also “cleans up” the fabric surface homogeneously, as a result providing good anti-pilling properties.

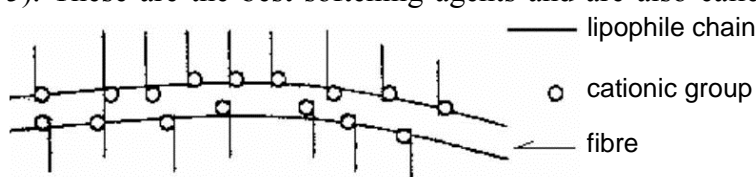
The best softness results can be obtained by carrying out the above mentioned physical-mechanical processes and by applying a special chemical softening agent.

As a general rule, the softening agents applied are hygroscopic or lubricating agents, which facilitate the fibre sliding within the fabric structure, thus granting easier deformation and creasing of the fabric. In most cases, the duration of the effect is limited since the products applied during the treatment are eliminated by subsequent washing; for this reason they must be applied in the final stage of the treatment. The most common softeners are detailed below:

Non-ionic softeners: generally ethers and polyglycol esters, oxiethylates products, paraffins and fats. These softening agents are generally less efficient than anionic and cationic ones but they withstand the effects of hard waters, acid or basic environment and also in presence of cations and anions, therefore the normal fabric care conditions.

Anionic softeners: sulphoricinates, anionic surfactants produced by the condensation of fatty acids. They have good characteristics as lubricating softening agents and give the fabric a full hand; they are unstable in hard water and acid environment. In addition, they must not cause yellowing at condensation temperatures.

Cationic surfactants: usually they are quaternary ammonium salts, amino-esters and amino-amides; they are recommended for all types of fibre, and can be also applied with exhaustion process in acid environment (pH 4-5). These are the best softening agents and are also called “molecular velveting” agents because they form bonds with the cationic group on the surface of the fibre generally with negative electric potential. They can give some problem in presence of large anions, and they can cause dye toning, or a reduction in



Picture 146 – Distribution of the surfactant on the

fastness to light values in the presence of direct and reactive dyes; they also have a high polluting charge as wastewater (bactericides).

Silicone-based softeners: these are generally polysiloxane derivatives of low molecular weight. They are insoluble in water, and therefore must be applied on fabrics after dissolution in organic solvents, or in the form of disperse products. They feature quite good fastness to washing. They create a lubricating and moderately waterproof film on the surface and give fabrics a velvety-silky hand (desirable for velvets, upholstery fabrics and emerised fabrics)

Reactive softeners: N-methylol derivatives of superior fatty amides or urea compounds replaced with fatty acids. The products have to be cross-linked and provide permanent softness and water repellency.

As explained previously, even though some softeners can be applied with exhaustion processes on yarns, when softening fabrics, the best technique is the continuous pad-wetting process followed by a drying stage in a stenter. This treatment must be carried out at the end of the finishing process; for this reason, softening is usually performed simultaneously with other dimensional stability processes (width stabilisation, weft and warp straightening). It is worth remembering that the use of softeners can reduce the fastness to rubbing of synthetic fibres dyed with disperse dyes, as the fatty surface layer tend to attract the dye molecules after hot treatments.

Crease-proof Treatments

Wash-and-wear and Permanent-press treatments

This chapter describes different finishing treatments as they are all carried out applying similar principles. Crease-proof treatments represent an outstanding results in finishing technology, since they give fabrics really new physical and/or chemical properties. The original aim of the researchers who first developed this process was to create a crease-proof rayon fabric; however, the new treatment was soon applied to cotton fabrics and linen cloths. The last generation versions of the treatment produce fabrics that are not only crease-proof when used but also preserve the crease effect if desired. This treatment can also ensure excellent results on cotton-synthetic blends (Permanent-press process.)

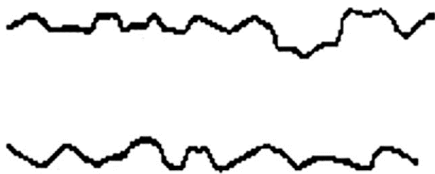
The auxiliaries used are synthetic thermosetting resins, or, more precisely, their monomers and their pre-condensates. The resins that react with cellulose are called "cellulose-reactants".

A certain crease resistance can be obtained by adding to fibres complex inorganic compounds of boron, as well as zinc and barium silicate. However, today the only products applied are synthetic thermosetting resins. The principle on which this finishing treatment is based consists of impregnating the fibres with resinogenic compounds of low molecular weight and cause afterward the formation of the resin in the fibres.

Recently new processes have been developed to chemically modify cellulose, aiming at improving the springback angle above all in wet substrates.

For a better understanding of what happens during a crease-proof process, it is worth explaining the mechanism and the reasons for which cellulose fibres tend to crease.

Cellulose fibres are made up of molecule chains formed by hundreds of thousands of glucose groups.



Picture 147 - Non-cross-linked polyglucose chains



Picture 148 - Polyglucose chains cross-linked with cellulose reactants



Picture 149 - Polyglucose chains cross-linked with thermosetting resins

The molecular chains of cellulose partly consist of crystalline areas rigidly oriented and compact, and partly of amorphous, loose and random-oriented layers; small covalence forces or electrostatic bonds cause their cohesion. By drawing the molecular chains, a stretching effect occurs due to the breaking of weak bonds and to the subsequent sliding of the single chains over each other, a phenomenon which becomes irreversible whenever the molecular chains (and therefore the cellulose fibres) assume a new position.

If we now suppose to transfer the drawing force and therefore the stretching of the external bending of a certain point in the fibre subjected to creasing, the bending angle will assume a permanent position as a consequence of the irreversibility of the phenomenon, therefore becoming a permanent crease.

Above all, cellulose fibres rich in amorphous areas and macromolecules, which tend to form bonds in the new positions imparted by mechanical stresses, can be affected by these deformation phenomena such as stretching, creasing and wrinkling.

On the contrary, fibres like wool – whose macromolecules are fixed by strong bonds (cystinic bridges or salt bonds) – as well as fibres with highly controlled intermolecular structure and high crystallinity degree (synthetic), will be highly crease-proof. It is

therefore evident and demonstrated the relationship between crystallinity, the presence of weak or strong bonds between the chains and the crease-proof quality of the fibres. In fact, while amorphous areas facilitate the sliding of macromolecular chains, the presence of weak bonds (hydrogen bridges) allow the stabilisation of macromolecules in their new positions and therefore the formation of a permanent crease. The above mentioned hypothesis lets us suppose that the replacement of weak bonds (electrostatic) with strong bonds (covalent) – i.e. capable of reducing the displacement of the chains and bringing them back to their original position when the bending force ceases its action or when substances blocking the sliding spaces are introduced in the intra-molecular voids of cellulose – can greatly improve the crease-proof properties of fibres. These pre-conditions are partly ensured by the so-called “amino-plasts”, as well as by cellulose reactants, which can form large-size molecules of resins, or bridges between the individual cellulose molecular chains, respectively.

Before the drying stage, fabrics are impregnated with precondensed amino-plasts of low molecular weight, or with cellulose reactant solutions. Before the 1990's, these solutions consisted of N.N-1.3dimethylol-4.5-dihydroxyethylenurea (DMDHEU) combined with magnesium chloride as acid catalyst, to improve the formation of cross-linking bonds between the molecules of cellulose chains.

The development of these bonds inside the amorphous areas of the fibre, improves the resistance to distortion and enhances elasticity properties; unfortunately the chemistry of N-hydroxymethyl (N-methylol) derivatives has a great drawback due to the reaction: $-H_2NCONH_2 + HCHO$, which produces free formaldehyde.

In fact, during the subsequent hot treatment which favours the formation of the resin, a bond with an hydroxyl of the cellulose ring sets individually, leaving an N-hydroxymethyl group non reacted and capable, following an hydrolysis process, of releasing formaldehyde, above all at high temperatures.

Another problem occurring when using these resins is represented by the chlorine absorbed by the textile material during the washing process, which cause a visible yellowing of the textile surface.

This does not represent an immediate damage, but when the textile is subjected to the action of heat

(ironing, calendering, steaming) it also loses a considerable part of its mechanical resistance.

<i>Properties of various resins</i> Dimethylol-urea				
dimethylol-urea (dmu)	dimethylol-ethylene-urea dmeu	dimethylol-dihydroxyl-ethylene-urea dm(oh) ₂ eu	dimethylol-dihydroxyl-ethylene-urea dm(or) ₂ eu	dimethylol-dihydroxyl-ethylene-urea (or) ₂ eu
non reactive	good reactivity	good reactivity	medium reactivity	medium/low reactivity
easily hydrolysab	stable to washing	stable to washing	highly stable to washing	sensible to hydrolysis
high chlorine retention	medium chlorine retention	medium chlorine retention	low chlorine retention	no chlorine retention
easily dry condensable	cross-linkable in dry and humid conditions	cross-linkable in dry, humid and wet conditions	cross-linkable in dry and humid conditions	only applicable by dry condensation
poor stability of treatment liquors	negative influence on fastness to light	no influence on fastness to light	low influence on hand properties	tendency to yellowing
high formaldehyde content	high formaldehyde content	medium formaldehyde content	low formaldehyde content	no formaldehyde content

Application techniques

Today, a number of treatments are available to give excellent properties to a wide range of textile products. The "wash-and-wear" finish is particularly effective since treated fabrics not only lose the creases formed on the dry fabric (i.e. when used) but also the creases which form on the wet fabric during manual or machine washing. The treatment to eliminate post-finishing creases is more complicated than the crease-proof treatment.

The cross-linking process can be carried out in three different ways:

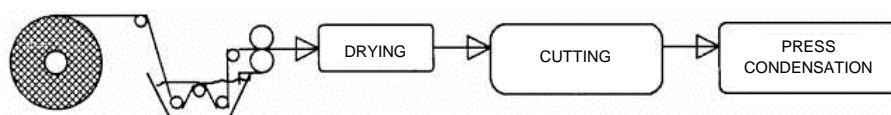
- 1. dry process:** with this method it is possible to obtain wide springback angles for dry creases and only medium springback angles for humid creases; dimensional stability and shape retention are excellent. The tearing and abrasion resistance loss is proportional to the dry crease angle, and are therefore generally high;
- 2. humid process:** the springback angles for humid creases are usually wide (proportional to residual moisture content), and dry ones are also good. Good dimensional stability and no-ironing properties (i.e. no ironing is required after washing). Low loss of tearing and abrasion resistance;
- 3. wet process:** optimum springback angles for humid creases, but very limited for dry creases. Good no-ironing properties and dimensional stability, with very low loss of tearing and abrasion resistance.

1 – Dry process

The classic process: the fabric is impregnated by means of a padding unit (the quantity of finish is tuned by modifying the liquor concentration and the squeezing ratio) and dried at 100-120 °C in a stenter; the cross-linking process occurs in the stenter, at temperatures varying according to the type of cross-linking agent used (generally 4-5 minutes at 150-160 °C). At the end of the process it is recommended to carry out a washing and softening stage (see STK process). Both self-cross-linking and reactive products can be used; ammonium salts or complex compounds are used as catalysts. It is a simple and quick process, as well as one of the most cost-effective. STK: drying and condensation are carried out simultaneously in a single run in the stenter at high temperatures (140 °C at the entry side, 180 °C at the exit side). The dwelling time inside the stenter depends on the products and the catalysts used, the temperature, and the substrate. This method is really cost-efficient but its results are quite uncertain and deterioration of the textile material may occur during the dwelling time in the stenter due to the high operating temperatures (resulting from the moisture variation in the fabric). For these reasons, STK is used above all for viscose. This process still requires a washing cycle to be carried out in order to comply with the strict regulations on formaldehyde fumes and the release of the metals contained in the catalysts.

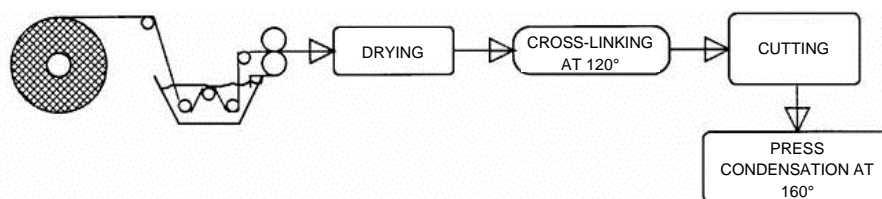
Double treatment: the fabric is impregnated with a softener and dried at 100- 130 °C. The procedure applied is the same as with the STK process. The application of softeners before the cross-linking or reactive agents provides excellent crease-proof properties and a limited loss of tearing and abrasion resistance. Permanent-press: the cross-linking step is carried out by the operator and gives good crease-proof properties and dimensional stability, and is therefore used to ensure shape retention for the finished garment. Two operating methods can be applied:

Post-curing: the fabric is impregnated with a solution of scarcely reactive cross-linking agents and special strong catalysts. Then the fabric is dried at low temperature and sent to the maker-up for cutting and ultimate making-up operations. Then it is hot pressed to assume the final shape and simultaneously obtain the cross-linking effect. (This method is scarcely applied due to the problem of formaldehyde fumes released and by non-washed fabrics or during storage.)



Picture 150 – The dry Permanent-press cross-linking process carried out with post-curing method

Post-curing for blends: used for fabrics containing at least 55% of synthetic fibres. The fabric is impregnated, dried, condensed and washed for stabilisation, to give a crease-proof properties to cellulose fibres and eliminate the free formaldehyde. After the cutting and making-up stage, a high temperature pressing stage will impart the final shape to the finished garment by exploiting the thermoplastic features of synthetic fibres.



Picture 151 - Dry Permanent-press cross-linking process with post-curing system for blends

The same method can be used on fabrics made of cellulose fibres only, using a combination of two cross-linking agents with markedly differentiated reactivity values as a wetting agent (see picture). A first cross-linking step is carried out on the fabric at low temperature (120-140 °C), while in the subsequent high-temperature pressing step (160-180 °C) the less reactive cross-linking agent will condense to set ultimate shape. (See the section on the post-curing method as far as formaldehyde is concerned.)

2 – Humid process

The fabric is wetted by means of a padding unit with a cross-linking agent and a catalyst solution; then 6-8% of residual moisture is removed from cotton (or 10-15% from other staple goods.) The fabric is then wound up on a roll, covered with a polyethylene sheet and left 16-24 hours to rest at ambient temperature. Strong catalysts must be used for this process and their quantity is tuned according to the residual moisture content. The final effect depends on the residual moisture: in case of low residual moisture content, the results will be similar to those obtained with the dry process whereas if the residual moisture content is high, the result is very similar to the cross-linking effect on wet substrates. The fabric hand after the treatment is generally soft. The fabric is then washed, the acids neutralised and the fabric is finally softened. Obviously this method does not allow continuous processing techniques, and therefore is not as common as dry cross-linking. However it ensures excellent results in wash-and-wear treatments, with low loss of resistance.

3 – Wet process

This process can be carried out in acid or alkaline environment. (The latter is less common as it gives limited crease-proof properties, though very low loss of tearing and abrasion resistance.) This method is similar to the previous one, except for the drying stage. The material is dried, wrapped, wound and covered with polyethylene and it is then kept rotating for 16-24 hours. The percentage of absorbed liquor vary considerably according to the type of processed fibres: Cotton: R.S. 100%, Polynosic: R.S. 120%, Staple: R.S. 200%.

Flame-retardant Treatments

The term inflammability refers to the ease of ignition and burning rate of fabrics. The flammability of fabrics (particularly drapery, textile covering and clothing fabrics) constitutes a danger in ordinary conditions of use.

<i>Textile fibre</i>	<i>L.O.I. (%)</i>
Wool	25
Cotton	18
Viscose	20
Acetate	18
Triacetate	18
Chlorofibres	48
Acrylic	18 – 20
Modacrylic	22 – 28
Polyester	20
Polyamide	20

The flame response of textile fibres is linked to their L.O.I. (limit oxygen index), which indicates the minimum quantity of oxygen a fibre needs in order to burn.

Given that the percentage of oxygen in the air is around 21%, it is clear that all fibres with an L.O.I. lower than this level will burn easily, while those with a higher L.O.I. will tend not to burn. From the table it can be seen that polyester, polyamide – both of these melt and form viscous masses – and cellulosic fibres are highly flammable. The latter, especially in less compact fabrics in which they have greater contact with the oxygen in the air, burn rapidly if heated to around 350°C,

temperatures at which they break down into highly inflammable volatile substances and carbonaceous residue.

The combustion mechanism and flame-retardant treatments

Cellulose exposed to high temperatures breaks down into flammable substances. Combustion of these products generates further heat, causing the cellulose degradation and breakdown process to continue until the cellulose has entirely disintegrated.

Cellulose combustion is a process that occurs in stages:

- 1) *Pyrolysis*: the action of an external heat energy source causes the homogeneous breakdown of the cellulose into liquid gas, tarry and solid products. The temperature at which rapid pyrolysis is triggered is around 300°C.
- 2) *Combustion of the gases produced*: at around 350°C the flammable vapours produced in the previous stage ignite, giving rise to a strongly exothermal oxidation reaction, which produces volatilisation, further pyrolysis and combustion of the liquid and tarry substances formed previously. From this point on, combustion proceeds spontaneously, resulting in the release of considerable heat, until such time as the cellulose material is completely burned up.
- 3) *Post-combustion*: when the tarry liquids produced in the first stage of combustion have undergone pyrolysis and combustion, a carbonaceous residue remains that undergoes slow oxidation (also exothermal) and continues to glow until it has been completely burned up.

To sum up, a fabric undergoing combustion will present the following zones:

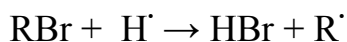
- a) a zone in which there are no longer any flames in evidence and in which combustion residue (ash) is present;
- b) a carbonaceous zone, glowing but flame-free;
- c) a burning zone: it is here that the violent oxidation of the gases produced (a series of reactions) is taking place;
- d) a zone in which it is possible to observe initial carbonisation and where the cellulose is undergoing the reactions of pyrolysis;
- e) an intact zone.

The theory of flame retardant systems

The action of flame retardants on cellulosic fibres can be explained in several ways:

- 1) *Through the formation of non combustible gases*, a result of the action of the heat on the flame-retardant product that has been added. These gases act in two ways: they reduce the concentration of combustible volatile substances, and they reduce the concentration of oxygen needed in order for the combustion process to continue. In decreasing order of efficacy, they act on the following gases: NH₃, HI, HBr, SO₂, CO₂, H₂O, and N₂. To achieve this end, the following substances are used: ammonium salts and organic nitrogenous compounds, like amine; b) organic halogenated compounds; c) salts containing high quantities of crystallisation water.
- 2) *Through catalytic action on cellulose dehydration*, in such a way as to obtain, at temperatures lower than ignition temperatures, a carbonaceous residue and to reduce the formation of flammable gases. This dehydration is catalysed by the acids.
- 3) *Through products that prevent the formation of anhydroglucopyranosium*. Since it is known that one stage in the pyrolysis of cellulose is the formation of levoglucosone, one need only block the hydroxyl groups in position 6 on the glucose molecule in order to reduce considerably the formation of flammable pyrolysis products. This objective is achieved by replacing the alcoholic function with the –O-SO₂-CH₃ group, with bromine, or by making the hydroxyl react with nitrogenous compounds
- 4) *Through the catalytic action of the derivatives of phosphorous* (phosphoric esters). These compounds reduce or prevent post-combustion of the carbonaceous residue. In the presence of phosphoric esters, the following reaction is favoured: $C + 1/2 O_2 \rightarrow CO + 26.4 \text{ Kcal}$, which is weakly exothermal in relation to the much more strongly exothermal reaction (94 Kcal) that leads to the production of CO₂. As a result, the temperatures reached in this case are low and the post-glowing phenomenon is absent. To achieve this objective, the following substances are used: ammonium phosphates, blends of phosphoric acid and amines, organic compounds containing phosphorous and ammonium.
- 5) *Through catalytic action inhibiting the oxidation of combustible gases*. Oxidation in the vapour phase is a process involving free radicals, some of the most important of which are the free radicals of H·, OH· and O·. The flame quenching action is often attributed to the capacity of the added substances to capture these radicals.

The action of bromine compounds, for example, is shown in the following scheme:



If the R^{\cdot} radical that is formed is less active than the H^{\cdot} radical, the result is inhibition of oxidation. In general, removal of the H^{\cdot} , the OH^{\cdot} and similar radicals by other less active radicals results in suffocation of the flame.

This is similar to the action of antimonium halides, compounds that are very efficient at capturing free radicals.

The main products used in flame retardant treatments of cellulosic fibres

Soluble inorganic products: ammonium salts, such as chloride, bromide and phosphate, applied in concentrations ranging from 10-20%, are very widely used. Borax, too, applied in concentrations of 6-10% and blended with boric acid (ratio 7:3) also confers good flame-retardant properties.

Soluble organic products: the substances used include ammonium sulphamate, phosphates, dicyandiamide, and thiourea.

Water-repellent treatments: these treatments are also relatively resistant to domestic washing and dry cleaning. They include the *Perkin treatment* (based on the deposition of stannum hydroxide). The cellulosic fabric is padded with sodium stannate, dried, treated with ammonium sulphate and dried again.

Treatment based on phosphoric acid and nitrogenous compounds: phosphoric acid, bound to the cellulose's hydroxyl group, has good flame retardant properties, however it reduces considerably the mechanical strength of the cellulose itself. To reduce degradation damage and improve flame retardancy, bases, like the ones listed here, are added: urea, guanidine, melamine, dicyandiamide, and nitrogenous resins such as urea-formaldehyde, melamine-formaldehyde (the latter also increase the solidity to washing of the product). A further improvement is obtained using phosphoric acid condensation products with the above-mentioned amines.

Of the various procedures proposed, the Bancroft procedure renders the flame-retardant property permanent to a degree. It consists of treating the cellulosic fabric with aqueous solutions of phosphoric acid-urea pre-condensate, applied by means of padding. This is followed by drying and by a thermal treatment. The latter, carried out at temperatures ranging from 140°C to 160°C enhances the condensation of phosphoric acid and urea and also fixes the condensate on the fibre as a nitrogenous phosphoric ester of the cellulose. The fabric is then washed thoroughly and dried. This flame-retardant product, which has low solidity to domestic washing, severely reduces the strength of the fabric and sometimes results in a change of colour.

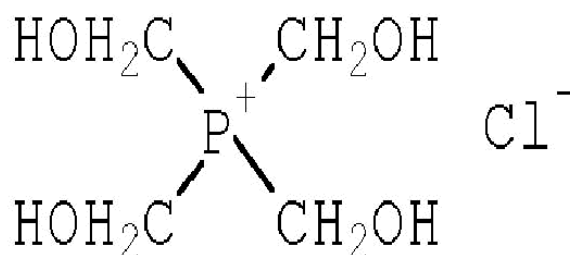
The treated fabric has good hand properties.

Permanent salt- or metallic oxide-based products: these derive from the union of metallic oxides with organic substances that are thermally unstable and have a high chlorine content (40-75%).

The metallic oxides can be: antimonium, arsenic, lead, zinc and stannum oxides, while the organic substances can be polymers of vinyl chloride, vinylidene chloride, chloroparaffin. The effect is lasting. This treatment is widely applied in the USA, where it is known as "F.W.W.M.R. Finish" (i.e., flame, water, weather and mildew resistant).

Antimonium trioxide (Sb_3O_3) offers little flame retardancy, unlike oxychloride and trichloride; the latter, however, through hydrolysis, release hydrochloric acid on fabrics, and this attacks the fibres.

Phosphorous-based products: in this family of compounds, tetrakis hydroxymethylol phosphonium (THPC) stands out in particular. Being without elements able to form non combustible gases, it is not used alone but rather with other flame-retardant products containing nitrogen or halogens (such as the azydirinic derivative APO) or with nitrogen compounds such as trimethylolmelamine or ureic resins with which it copolymerises.



THPC

One process that has a particularly important application is the Proban process. This process exploits the copolymerisation of THPC and methylolmelamine to form a highly flame-repellent resin that contains phosphorous and nitrogen. The two products are dissolved in the same liquor to which triethanolamines are added as stabilising agents and urea as a buffer agent. The effect is permanent and, provided there is not too much alkali present, not affected either by domestic or industrial washing. The most difficult part of the application of this treatment is the final polycondensation, which demands well ventilated equipment and perfectly controlled treatment times, otherwise the mechanical strength of the fabric is severely jeopardised.

THPC-urea process (or process with melamine, dicyandiamide or guanidine). The fabric is impregnated with THPC and one of the above-mentioned nitrogenous substances, after which it undergoes a thermal treatment. It is dried, treated with ammonia, rinsed and dried again. A good and wash-resistant effect is obtained.

Hydrophobic, Oil-proof and Water-proof Treatments

Waterproofing is a treatment that does not allow water or air passing through the fabric. It consists of the application of substances capable of forming a thin waterproof layer, eliminating any space between the fibres and yarns in the fabric.

The hydrophobic treatment gives the fibre the ability to repel water, but not air and water vapour. This treatment does not clog the fabric pores but reduces the capillarity effect by coating the textile substrate with substances having a low surface tension.

The stain-proof treatment makes the fabrics hydrophobic (thus avoiding aqueous substances to penetrate them) and oil-proof (which limits or prevents the penetration of fatty substances).

Wetting of the textile substrate

We will now try to explain why a textile surface becomes wet. The natural hydrophilic characteristics of fibres greatly facilitates all finishing processes, and dyeing in particular, but this property can represent a problem under certain conditions, e.g. soiling caused by water or oil soluble substances, or when protecting a person during outdoor work or even when the fabric must withstand harsh weather conditions.

It is therefore crucial to get a better understanding of these phenomena to improve the water and oil repellency of textile substrates, above all when they are destined to special uses (for example working garments.)

Since it is impossible to modify the basic chemical structure of fibres or eliminate the porosity typical of textile products, it is important to modify surface and chemical structures.

The wetting of a textile substrate produces a three-phase modification (solid, wetting fluid, air), generating simultaneously surface and interfacial tensions.

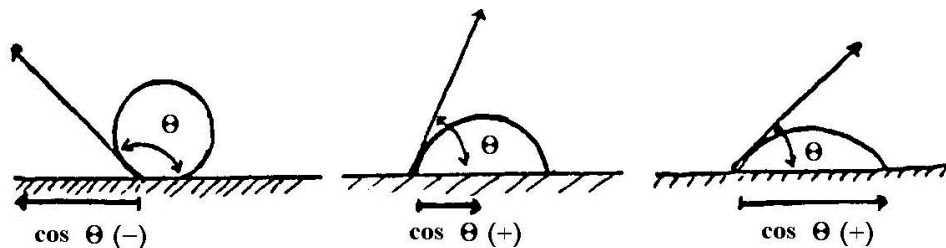
Let's imagine a drop of liquid substance deposited on a solid surface: the attraction forces between its molecules allow the drop to keep its spherical shape.

If great attraction forces generate from the solid surface in contact with the liquid (i.e. in case that the solid has a great surface energy), the surface tension of the liquid is not sufficient to keep the spherical shape: the drop consequently spreads on the surface and becomes more similar to a flat lens. Then it adheres to the surface and wets it.

To cause the surface of a solid not to be wetted by a liquid, the surface energy of the solid must be inferior to the surface tension of the liquid.

A liquid therefore adheres to a solid because of the attraction forces originating from the molecules of the surface of the liquid and of the solid (interfacial tension) and is independent from the underlying molecular layers.

Wetting can be evaluated by measuring the contact angle formed by the intersection of the surface of the solid and the tangent of the arc surface of the drop. This angle is indicated with the symbol θ (theta).



Therefore:

If the surface can be wet, we will have $\theta < 90^\circ$ and $0 < \cos \theta < 1$;

If the surface is scarcely wettable, we will have $\theta > 90^\circ$ and $-1 < \cos \theta < 0$.

Since the tendency of the liquid to wet a solid is inversely proportional to the contact angle, $\cos \theta$ becomes a direct measure of the wetting property.

Wettability and penetration of a liquid through a fabric

Along with the above mentioned criteria, it will be worth considering that the surface of the fabric is more or less rough and therefore greater than its apparent surface. The value of $\cos \theta$ (which expresses the wetting ability) must be therefore multiplied by the roughness factor "r" (with $r > 1$), and therefore the tendency of the fabric to wet becomes proportional to $r \cos \theta$.

This relationship shows that if a smooth surface can be excellently wetted, its roughness will improve its wetting ability while if a smooth surface can be wetted with difficulty, its roughness will render it even less wettable.

The diameter and the distance between the yarns of a fabric are also very important and must be carefully evaluated in waterproof and oil-proof applications.

On a perforated surface like that of a fabric, liquids form contact angles which increase in proportion with the ratio $r + (d / r)$ (Cassie and Baxter relation) where:

“r” is the yarn diameter,

“d” is the distance between two fabric threads.

Furthermore, the liquid in contact with a porous solid like a fabric, tends to penetrate it like a capillary fringe, up to a height (h) depending upon the surface tension of the liquid (γ_L), its density (ρ), the radius (r) of the capillary fringe and the angle of contact (θ) between the liquid and the solid:

$$h = K \gamma_L \cos \theta / r \rho$$

Therefore, when the angle of contact is smaller than 90° ($\cos \theta > 0$) the liquid will show a capillary diffusion into the solid.

Once the liquid has penetrated the fabric, the surface tension of the liquid no longer contrasts the flowing of the liquid and a stable flow will establish. Generally speaking, a fabric that has been made water repellent can better stand wetting and water penetration if yarns are small and the weave is thick.

Hysteresis of the angle of contact

The angle of contact (θ) reduces by increasing the contact between the liquid and the solid. It is therefore necessary to underline the difference between: the advancing angle (formed by a drop in contact with a dry surface) and the receding angle (formed on a surface previously in contact with the liquid).

The difference between these two values is the hysteresis of the angle of contact. The higher the hysteresis, the poorer the tendency of the liquid to “pearl” (i.e. to slip on the surface of the fabric by forming separated droplets), notwithstanding the high advancing angle. This is an important factor to be considered, for example in materials that will be exposed to rain and on which, after a certain period of time, the pearling effect no longer occurs. The hysteresis of the angle of contact is higher when the fabric is wet with water than with organic liquids. A specific material after the flame retardant treatment must have high receding angles (at least $>90^\circ$).

Porous solids, like textile substrates, have a water receding angle that decreases very rapidly according to the period of immersion. For example, the pearling effect will disappear and water will form a continuous surface film if a fabric is exposed to the rain action for a certain period of time.

The supremacy of silicones compared to other waterproofing agents is due to the slow decrease of the receding angle rather than to a high angle of contact.

In case of surface contact between the fabric and water, the hysteresis of the contact angle can be originated by different reasons:

- formation of a hydrous layer on the surface of the solid, due to water or water vapour absorption;
- solubilisation in water of part of the hydrophobic substances (or mechanic removal),
- the breaking of an hydrophobic film and the subsequent fibre hydration,
- orientation inversion of the hydrophobic film, which (in contact with water) directs polar groups towards the surface.

Hydrophobic treatments and products

For the above mentioned reasons, to avoid the wetting of the surface of a macromolecular and porous material like a fibre, the surface must be covered with a film formed by a substance with a surface tension that is smaller than the textile.

In this way the drops of water will assemble on the surface, isolated from each other, to create the pearl effect.

A waterproof effect can be also obtained by using non-filmogenic substances that form a sort of "brush" of short molecules. By limiting the formation of a hydrophobic state on the surface of the textile substrate, the basic properties of mechanic resistance and flexibility of the fibres remain unaltered. If also swelling (mainly due to the presence of amorphous areas) must be strictly controlled, these amorphous areas can be filled with macromolecular resins.

Both polymer and low chain water-repellent products should have essentially a hydrocarbon character (with groups having a lower surface tension such as =CH₂, -CH₃ or perfluorinated chains), to reduce the surface tension of the fibre until making it water-repellent.

Method based on emulsions in single bath

This method is recommended for producing awnings or camping tents and umbrellas but it does not stand washing in water and solvents. The size of the emulsion particles must range within 0.1 and 2 micron, and can be stabilised, or not, by using protective colloids (hide glue, cellulose ethers, polyvinyl alcohols). The textile substrate treated with this method is dried in stenters at 80-100°C. Good results can be obtained with medium-weight/light fabrics made of cotton, cotton-synthetic blends and wool, with a good cost-efficiency ratio. Unfortunately the waterproof finish is not a durable one. Better results for waterproof ability and solidity to usage and washing can be obtained by replacing Al salts with Zr salts (ammonium and zirconium dicarbonate, zirconium oxychloride, etc.), by applying them on fabrics made of cotton, cotton-synthetic blends and wool, with a technique similar to the above mentioned one. Good results can also be obtained on cotton, blends and wool, by using chromic chloride stearate emulsions with or without colloids, in presence of examethylene tetramine, by padding the fabric, drying it and polymerising at 130°C for 3 minutes.

Durable methods

It is possible to bind hydrophobic chains to cellulose fibres by reacting the primary hydroxyl groups (etherification, esterification, etc.); the waterproof values reached are generally poor, but durable, since they do not cause the formation of the surface film.

The results can be remarkably improved when these products are combined with resins.

Usually the fabric is wetted by dispersing the product; the fabric is then dried and treated at 90-120°C.

Products made of resins linked to fatty acids

These products feature excellent solidity when washed in water at 60-90°C, though not when washed with solvents. They are recommended for treating raincoats, uniforms etc. It is possible to use methylol-ureastearamide derivatives, ether alcohols superior to dimethylolurea, but more frequently melamine derivatives linked in different ways with lipophile chains. These products (whatever their formulation) can be used for padding applications in the presence of acid catalysts (ammonium chloride, ammonium nitrate, aluminium chloride or zirconium oxychloride), dried and polycondensed at 140-150°C. It is important that fabrics made of synthetic fibres dyed with dispersed dyes, are dried at low temperatures after the padding process; this prevents the dyes from migrating toward the hydrophobic surface and maintains the fabric's solidity to rubbing.

Silicones

These products are stable to washing in water at 60°C with solvents. They can be used to treat uniforms, raincoats and sportswear. These products are very popular since they allow excellent waterproofing properties, optimum solidity (that can also be enhanced if combined with resins) and a very pleasant and soft hand (they are also used as softening agents.)

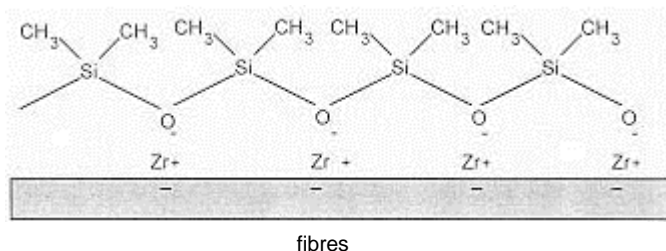
Starting from silicon and chloromethane, or from silicon tetrachloride with Grignard reagent, they are made react with water to release silanols.

The dimethylsilanols obtained in this way can polycondensate in acid environment by forming linear dimethylpolysiloxanes.

Precondensed products with low molecular weight are generally available on the market as solutions (in organic solvents such as carbon tetrachloride or n-decane) or contained in aqueous emulsions; they are recommended for completing the condensation process on fibres at 140-160% or in milder solutions for longer times (acid hydrolysis of cellulose is avoided with a loss of tenacity) by adding special catalysts (Zr oxychloride and Zn nitrate).

They are suitable to be applied on all types of fibres and also on emerised or coated fabrics.

The high water-repellent effect and the soft hand are due to the orientation toward the outer surface of methyl groups induced by positive Zr ions linked to the negatively charged fibres:



Fluorinated products

They feature an excellent fastness to washing in water and solvents. They are suitable for treating uniforms, raincoats and sportswear, tablecloths and protection clothes (after washing they must be ironed to recover their original effect).

These products are resins bound with hydrocarbons having at least the last four atoms of C perfluorinated.

These products allow excellent waterproofing results also with oil-repellency properties (if stains have not been pressed onto the fabric.)

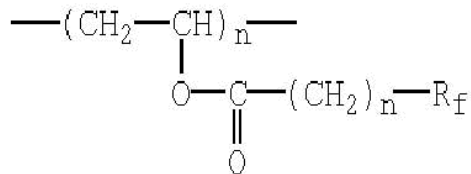
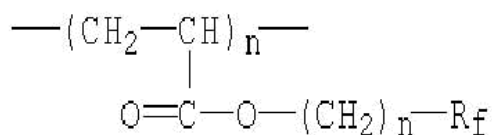
The application is carried out by padding the fabric, which is then dried at 100-120°C and subsequently polymerised at 140-150°C.

Stain-proof treatment

This treatment is often combined with waterproofing and other finishing treatments, and is particularly indicated for synthetic fabrics (oil-wettable) and synthetic blends, but it can also be carried out on all types of fibres.

The stain-proof treatment bases on the application of molecules having hydrocarbon chains of at least 4 atoms of perfluorinated carbons, included the last one. These chains must be homogeneously distributed on the surface of the fibres and must represent at least 1% of the weight of the textile substrate. The most commonly used products are based on perfluorinated esters resins of acrylic acid and/or perfluorinated esters of polyvinyl acid, which make the fabric hardly wettable with oily and aqueous fluids. Furthermore the presence of fluorocompounds makes it easier to remove oily stains with solvents, by shrinking the stained area and avoiding the formation of halos.

Rf = Perfluorinated chain



Anti-soil Treatments

Hydrophilic fibres (both natural and man-made), when non-treated, are considered easy-wash materials, which, moreover, do not absorb dirt during washing. This is to be attributed to the fact that they have a very high critical surface tension in air, and thus a very low interfacial tension in water. On the other hand, certain synthetic fibres (particularly polyester), like cellulose fibres that have undergone chemical finishing processes (based on silicones, fluorocarbon compounds, permanent-press or wash-and-wear resins and acrylic resins), are difficult to clean because of their highly water-repellent surfaces. These surfaces produce an accumulation of electrostatic charges, and thus absorb and retain dirt.

Clearly, therefore, there is a need for treatments that reduce the natural build-up of dirt with use - a treatment that is applicable to any fabric and that allows it:

1. to repel dirt during use (i.e., that makes it soil and stain repellent);
2. to be cleaned easily through normal cleaning procedures (brushing in the case of carpets, washing in the case of shirts, etc.) (i.e., that confers soil-release, easy-wash properties);
3. not to take on, during washing, that greyish/yellowish hue that is due to the re-depositing of soil particles from the dirty water (anti-soil redeposition).

There is no type of finishing treatment that can confer, at the same time, all these properties on a fabric. Indeed, in some cases, a finishing treatment that confers one of the aforementioned properties, reduces the performance of the fabric where the others are concerned. Thus, the choice of an anti-soil treatment must be governed by the extent to which the article is effectively likely to become soiled – and this of course depends on its destined use.

For the sake of simplicity, the substances liable to soil a fabric can be subdivided as follows:

- solid particles. The fabric will occasionally come into contact with fine particles capable of soiling it (soot, rust, blends of organic and inorganic substances).
- oils and greasy substances;
- water-soluble substances (natural colorants present in products such as coffee, wine and ink).

There are five different ways in which these substances can come into contact with the fabric:

- 1) through direct transfer (contact);
- 2) through the deposition of airborne substances (solid particles that, because of their density, fall onto the fabric or that, because of its electrostatic charges, are attracted to it);

- 3) through the deposition of substances contained in solutions or aqueous suspensions (solid particles, for example mud particles, or particles present in oily or coloured liquids). This category also includes the dirt contained in dirty washing liquor, which, despite being extremely diluted, can redeposit extremely fine soil particles deep within the fibre. Furthermore the high temperature of the liquor can favour the penetration of certain soil particles and even fix others in the fibre;
- 4) through transportation via oils and greases (greasy substances, but also solid transported substances, such as those present in lubricants, or coloured substances, like those contained in lipsticks);
- 5) through deposition of substances contained in solvents. Garments washed using dirty solvents can retain the soil particles they contain.

Fibres can retain solid substances (dirt) in a number of ways:

- by macro-occlusion or the trapping of particles between threads or fibres.
- by micro-occlusion of the smallest particles in irregularities present on the fibre surface. Since the size of these irregularities is below 50 μm , only soil particles of a similar size are trapped.
- by absorption at the level of the fibre surface, due to Van der Waals and Coulomb forces.
- by solubilisation or absorption of oily substances deposited on the fibre. This is associated, above all, with synthetic fibres.
 - by bonding to the finishing agent on the fibre, especially plastic or soft resins.
 -

The ease with which dirt is eliminated or absorbed is influenced considerably by the geometry of the fibre and yarn. Indeed,

- round-section fibres soil less and come cleaner during washing;
- curly staple fibres, with an irregular section have an increased tendency to absorb and retain dirt;
- dirt easily penetrates – but is also easy to eliminate from – yarns that are loosely twisted, whereas the dirt that penetrates more tightly twisted yarns is more difficult to remove;
- very highly twisted yarns show very little susceptibility to the penetration of dirt.

PRE-SOIL treatments

Solid particles of dirt are deposited on fibres, adhering mechanically to their rough surfaces: those involved in the first stage of fabric soiling find their way into the pores, producing a colour that is very difficult to get rid of; on the other hand, those that are absorbed subsequently (i.e., once the fibres' pores are full) can be eliminated through simple mechanical actions.

If, therefore, a finishing treatment is used that fills in the fibre's surface irregularities (pores, indentations, holes) with white and translucent particles, the dirt that is subsequently deposited will inevitably adhere only superficially and thus be removable through the application of normal cleaning techniques (brushing, vacuum cleaning).

However, the diameter of these "pre-soil" material particles must correspond to that (0.05-0.2 micron) of the irregularities present in the fibre, as larger particles would afford only temporary protection.

Of the products that have been applied in practice, particularly in the treatment of carpets, some, in particular, have given successful and durable results. These include: oxide blends, such as zinc aluminium, magnesium, iron, and aluminium phosphate blends, all applied by means of sprays, padding or exhaust processes. The disadvantages of this treatment are

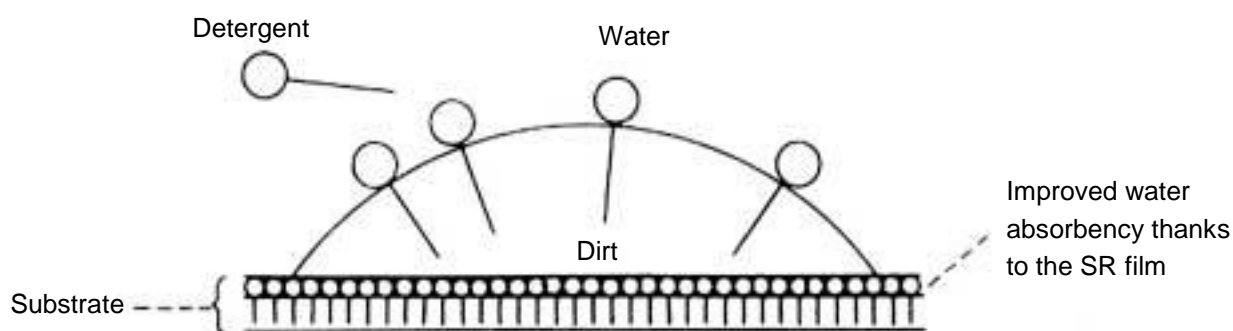
uncontrollable dust formation and, if a continuous film forms, a hardening and worsening of the hand.

SOIL RELEASE treatment

The expression Soil Release refers to the capacity to release dirt through wet cleaning. The aim of this finishing treatment is not to prevent a textile from soiling, or to reduce its tendency to absorb dirt, but rather to facilitate the removal of dirt through wet cleaning.

Soil Release finishing treatments are used, in particular, in the polyester curtain sector and in the production of other textiles destined to be made up into household linen or underwear. While Soil Release finishing treatments are only rarely applied to polyamide or acrylic fibres, they are more often used on blended goods (wool/acrylic fibres), destined to be made up into items of women's clothing.

The Soil-Release finishing treatment is based on a process that enhances the hydrophilic properties of the fibres in such a way that the dirt, particularly water-repellent dirt, passes more easily into the water during domestic washing cycles. The figure below illustrates, in this regard, the relationship that is established between dirt and detergent during wet cleaning: the longest part of the detergent molecule (the hydrophobic, unipolar part) becomes oriented towards the dirt, while the hydrophilic (polar) part remains free in the aqueous medium.



Picture 152 - Diagram of the effect produced by the Soil Release finishing treatment

As shown in the diagram, the Soil Release effect is obtained through the use of a chemical that has the capacity to form, on the surface of a fabric, a film (SR) that is able to reduce the attraction of the dirt towards the hydrophilic surface of the textile and, at the same time, to facilitate the introduction of the washing liquor between the dirt and the surface of the textile.

The chemical products found to be best suited for this particular use are ones that have the capacity to form a thin film – that is not sticky and that does not present plastic properties in the presence of heat – of negative charges on the surface of the fabric.

What is more, these products are able to confer an anti-static effect, which also favours the release of soil: the accumulation of electrostatic charges is, indeed, one of the main reasons why airborne particles are retained by synthetic fibres (the latter, through electrostatic mechanisms, attract them and bind them to the fabric).

These products are emulsions, based on polymers or copolymers of acrylic or metacrylic acids, or on the relative salts, as well as on additional ethylene oxide compounds, and fluoride compounds. All are particularly resistant to wet cleaning, providing a metallic salt catalyst is used in the application stage.

Anti-static Treatments

Being characteristically hydrophobic, synthetic fibres present a low electrical conductivity, so low that, after rubbing against other bodies, they can retain an electrical charge for a long time. Indeed, when two bodies, characterised by a neutral electrical charge and each having a different chemical composition, are rubbed together, the electrons of each of them will attract those of the other in such a way that both bodies acquire an electrical charge.

Generally speaking, the body with the higher dielectric constant takes a positive charge, while the substance with the lower dielectric constant takes a negative one.

A potential difference, of as much as several hundred millivolts, is created between the two contact surfaces.

If these two bodies, both charged with electrical energy, are separated, the potential is increased, even as high as many tens of thousands of volts.

As far as fabrics are concerned, this discharge of energy occurs mainly between the innumerable fibrils. It is responsible for creating the familiar crackling sound and for the formation of the tiny sparks and the genuine electrical discharges that can cause perceptible discomfort. To reduce this phenomenon, one can operate in a controlled environment that has high relative humidity, use conductors that can discharge the material, ionise the atmosphere, or apply hydrophilic chemical substances. Chemical products that confer an anti-static effect on synthetic fibres form, on the fibre surface, a thin film whose electrical conductivity is higher than that of the fibre.

These substances are anionic, cationic, amphoteric, or even non ionogenic. The conductivity of a synthetic fibre is thus increased when it is covered with a surface-active substance in which the hydrophobic groups are oriented towards the fibre and the hydrophilic groups are oriented away from it.

The presence of mobile electrical ions is, however, important.

Depending on the substantivity of the chemical products used, it is possible to choose between different application processes: immersion, exhaust or padding.

Anti-static finishing treatments are rarely applied through spraying. Chemical products that have the capacity to confer a permanent anti-static effect condense at high temperatures; they can even condense when stored at ambient temperature in hermetically sealed rooms or containers (as can epoxy resin-based products).

All the anti-static products available on the market can be applied by padding, while only a few can be applied using the exhaust process. The material is immersed in liquor containing the anti-static chemical product, squeezed (to 40-60% absorption) and finally dried in a stenter at 80-100°C.

If the stenter is equipped with additional chambers that can be used to carry out heat setting processes, then it is also possible to condense, at the same time, anti-static products able to confer permanent effects.

Anti-mildew Treatments

In certain ambient (humidity and heat) conditions, cellulose can be permanently damaged. This damage can be due to depolymerisation of the cellulose or to the fact that certain microorganisms (mildews) feed off it. The situation is worsened, during long storage periods, by the presence of starch finishing agents.

This damage can be prevented by the use of antiseptics, bacteria controlling products containing quaternary ammonium salts, and phenol derivatives. Dyestuffs containing heavy metals can also act as antiseptics. Permanent modification of the fibre (cyanoethylation) is another possibility.

Antimicrobial Treatments

In principle, antimicrobial treatments for fabrics work by limiting the growth of the microorganism population. This also leads to a reduction in the quantity of unwanted by-products. The active principles that limit the growth of the microorganism population are known as "antimicrobials". Here, a distinction can be drawn between those that have a bacteriostatic effect, i.e., that limit growth, and those that have a bactericidal (or lethal) effect.

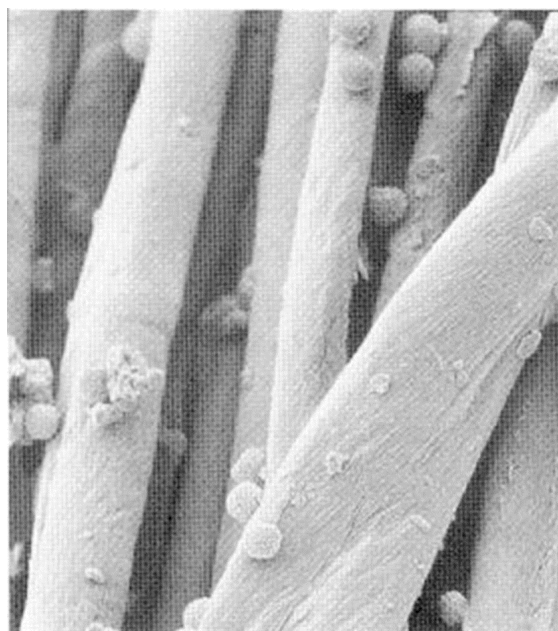
The former have the following aims:

- to prevent the transmission and propagation of pathogenic microorganisms (hygiene sector);
- to reduce unpleasant odours due to bacterial degeneration (deodorisation);
- to prevent loss of an item's suitability for use (as a result of decomposition of fibres following attack by microorganisms).

There are various chemical and physical possibilities that can be considered in the production of antimicrobial fabrics. In practice, the antimicrobial effect is obtained through the application of specific chemical products during the finishing stage, or through the incorporation of these substances into chemical fibres during the spinning process.

These possibilities are:

- the addition of bactericidal substances to the spinning solution, prior to the extrusion stage – substances like Triclosan (2,4,4-hydrophenyl trichloro (II) ether), a member of the antiseptic and disinfectant family. Triclosan is a halogen-containing derivative of phenol, and is used in cosmetics and toothpastes. It has a wide range of action against gram-negative and gram-positive bacteria. This compound, thanks to the presence of the acaricide benzyl benzoate, also offers protection against mites and is used in acaricide (spray or powder) formulas, as well as in a solution (25% concentration) for the treatment of scabies. This compound is non toxic. Benzyl benzoate is an acaricide that acts, chemically, directly on the mites.
- A different method for the production of antimicrobial and fungicidal fibres has been adopted by an English company. Its "Stayfresh" fibres exploit the properties of silver and silica, both of which, on coming into contact with water or humidity, arrest the growth of bacterial populations in carpets, fabrics, furniture, mattresses and bed linen, by cutting off a source of their nutrition. As well as having antimicrobial and fungicidal properties, these fibres are safe, non toxic and inorganic because,



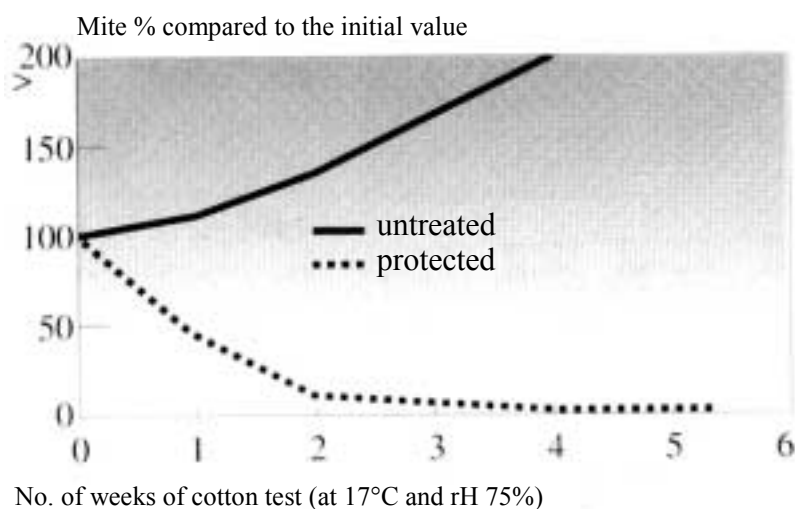
Picture 153 - Allergen-containing house mite excreta on fibres are initially covered in a mucous layer. This layer is subsequently broken down into tiny particles.

they guarantee total mildew and fungus control, preventing the propagation of bacteria such as *Escherichia coli* and *Staphylococcus aureus*.

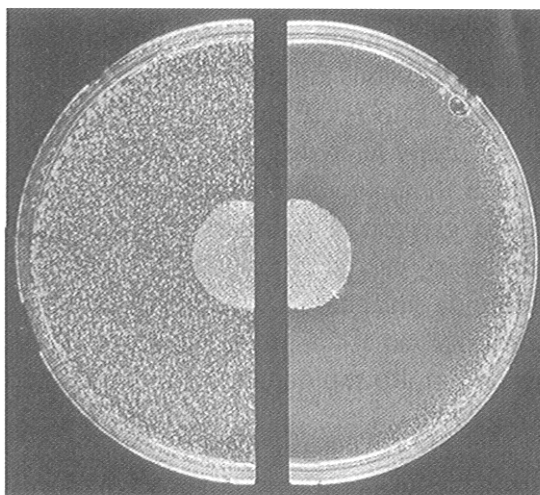
- Modification through grafting or other chemical reactions. It is in this sector, that the Institut Textile de France in Ecully has developed the so-called biotextiles. In these products, the chains of molecules containing antiseptic substances are grafted onto the base polymers of the raw fabric. The base polymers are activated by electronic rays and, in the course of the process, they are refracted in given positions, into which is inserted the first graft molecule. The chains of polymers, which grow laterally from the first molecule, confer on the fabric its bactericidal properties. In the event of direct contact, these fabrics act very rapidly against bacteria and their bactericidal property remains intact even after washing.
- Fibre blends.
- Textile finishing treatments with specific active principles. Following heat treatment (drying, condensation), these substances, being incorporated into polymeric and resinogenic finishing products, become fixed to the structure of the textile.

Antimicrobial finishing products

Man has adopted antimicrobial substances since ancient times, a fact that is demonstrated by their use in Egyptian mummies and in similar applications in other cultures.



In this regard, the protection and preservation of fabrics, too, have long fulfilled a role of the utmost importance. The need to protect and preserve is still fundamental in many textile applications today. "Antimicrobials" are protective agents that, being bacteriostatic, bactericidal, fungistatic and fungicidal, also offer special protection against the various forms of textile rotting. The main antimicrobials include phenolic active principles, quaternary ammonium salts, and organic-metallic (Hg) compounds. The chemical products listed in the table on page 156 can be used to obtain antimicrobial effects in fabric finishing and in the production of chemical fibres. A different method for the production of antimicrobial and fungicidal fibres has been adopted by an English company. Its "Stayfresh" fibres exploit the properties of silver and silica (silicic acid), materials that react with water and humidity, cutting off a source of nutrition of the house mite and shrinking its population.



Picture 154 - Specific treatments create a zone in which bacteria cannot proliferate, as the test in the picture demonstrates

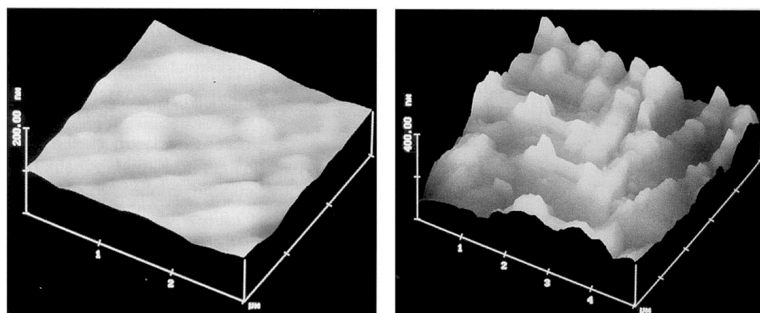
Antimicrobials	Materials
Aniline	3,4,4-trichlorocarbaniline
Phenol	Biozole, thymol, sodium alkylbisphenol salt
Guanidine	1,1-examethylene up to 5-(4-chlorophenyl) diguanide digluconate; diguanide polyexamethylene hydrochloride
Imidazole	2(4-thiasolil)benzimidazole, benzothiazole
Inorganic compounds	Silver zeolite; titanium oxide; silver silicate; silver sulphate; ferrous phtalocyanate; copper sulphate
Natural products	Glucosane; propolis; hinokichiole
Surfactants	cloruro di poliossilalchiltrialchilammonio - Organic silicone with tertiary ammonium salt; octa-decidimethyl(3-trimethoxypropyl, ammonium chloride). Tertiary ammonium salt: didecilmethylammonium; exadecilperydium; cetyldimethylbenylammonium; polyoxylalkyltrialkylammonium

Plasma Treatments

Plasma treatment is a surface modifying process, where a gas (air, oxygen, nitrogen, argon, carbon dioxide and so on), injected inside a reactor at a pressure of approximately 0.5 mbar, is ionised by the presence of two electrodes between which is a high-frequency electric field. The need to create the vacuum is justified by the necessity to obtain a so-called cold plasma with a temperature no higher than 80 °C. This, with the same energy content that can be reached at atmospheric pressure at a temperature of some thousands of degrees C, permits the treatment of fabrics even with a low melting point such as polypropylene and polyethylene, without causing any form of damage.

The fabric, sliding through the electrodes, is subject to a true bombardment from the elements that constitute the plasma (ions, electrons, UV radiation and so on) and which come from the decomposition of gas and contain a very high level of kinetic energy.

The surface of the fabric exposed to the action of the plasma is modified, both physically (roughness), as well as chemically, to remove organic particles still present and to prepare for the successive introduction of free radicals and new chemical groups inside the molecular chain on the surface of the material. The mechanical properties remain, on the other hand, unaltered, as the treatment is limited to the first molecular layers. The working process is dry,



Picture 155 - a) A nonwoven substrate before plasma treatment
b) The same nonwoven substrate after plasma treatment.

environmentally friendly and inexpensive; a fabric is normally treated at a speed of 13-20 m/min, with a consequential time of exposure to the plasma of around 30-40 seconds, using as mentioned above a gas (in the majority of cases it is air) and electrical current. The tension during the winding of the web is controlled by a load cell capable of maintaining the tension previously established, even though this is very low; it follows

that also with "melt-blown" type fabrics which generally have the lowest tensile strength can be successfully adapted. The fabrics treated with plasma present a high superficial energy, assuming however high hydrophilic properties, though they are originally water repellent. This permits on the one hand the elimination or the limitation of solvents in the successive processing steps, on the other it makes the chemical products used for finishing more efficient for the best and most uniform deposit of the product itself and for the adhesion of a chemical type between the active group present on the surface of the fabric treated and the coating product.

It is possible therefore to obtain anti-static, antimicrobial, stainproof or flame retardant fabrics, with clearly higher performance, with better resistance to washing and wear and tear, and with finishing that is at times more simple and less expensive.

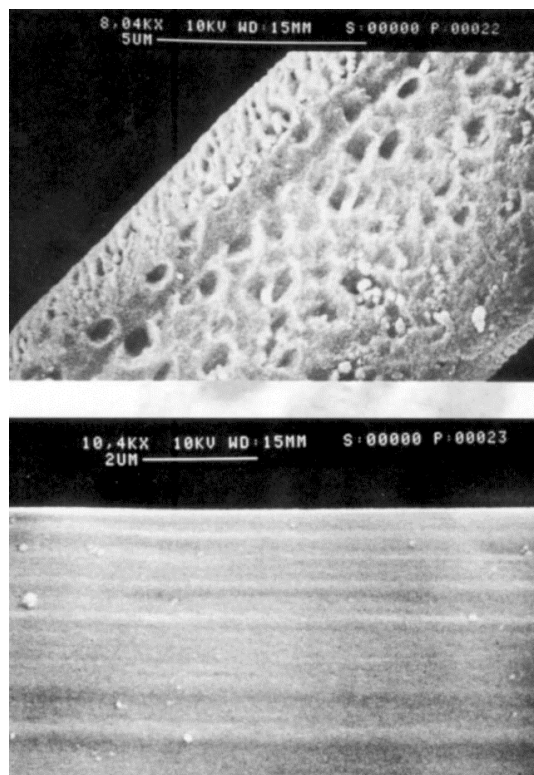
The resistance to peeling and fibre-matrix interface resistance, which are the fundamental characteristics typical of multilayer products such as:

- composites (e.g. Kevlar, glass, carbon/epoxy resin or polyester),
- laminated textiles (e.g. fabric/nonwovens, fabric/film),
- coated textiles (e.g. fabric/resin or polyurethane foam)

is much higher than the values of the same products obtained without plasma treatment. In fact, for fabrics made from natural and man-made fibre, the plasma treatment also improves dyeability characteristics, such as intensity (approx. 30%) and solidity (I point), and in particular, for animal fibres, it confers strong anti-felting characteristics. This means that the chlorine process can be avoided and therefore so too are the damaging physical properties this creates for the fabrics themselves, but also for people and the environment, as chlorine is a pollutant.

The effects of this plasma treatment on surfaces are significant and uniform along the length and width, and they last a long time. The increase in surface energy of the fabrics means that chemical products containing solvents can be entirely eliminated from the conventional process necessary to uniformly wet the fabric surface. Furthermore, as the plasma treatment is efficient only on a level of the first surface layer, no damage to the physical properties intrinsic to the textile are noticed.

It follows from the very interesting applications of the plasma treatment that also applications of nonwovens have become apparent, having a destination of use among other things in air and liquid filtering, synthetic leather, cloths, artificial limbs, biomedical and protective wear, footwear and sportswear.



Picture 156 - Silk fibre treated with nitrogen plasma (above) and not treated (below).

Enzyme Treatments

This chapter aims to propose and develop, though in a summary form, the enormous possibilities and advantages, of an environmental and ecological nature, deriving from the use of enzymes in various textile finishing operations as an alternative to traditional processes and chemical products.

Enzymes are proteins formed by long linear chains of amino acids linked by peptidic bonds. They are present in all living cells which carry out vital functions in the metabolic process, of growth and cellular reproduction, transforming and conserving energy. They are biological catalysts capable of notably accelerating the chemical reactions which occur in living organisms. They are produced by cells, but they are not viruses or bacteria and they cannot reproduce autonomously; they are therefore "alive" even though not biologically active, in determined conditions of pH, temperature, liquor composition and so on.

In the past, enzymes used industrially were obtained by:

- extraction and purification of animal organs or tissues (pancreatic trypsin) or from vegetal sources (papaine);
- techniques of fermentation of selected microorganisms (bacterial amylase).

The latest developments in genetic engineering and bioengineering have totally revolutionised the technological scene widening the outlook for the types of applications and expanding the enzyme market. In particular, protein bioengineering has permitted:

- the adaptation of biochemical characteristics of an enzyme under conditions of the industrial process;
- the creation of new enzymes with catalysis techniques which do not exist in nature;
- the alteration of the properties of enzymes such as stability, activity, composition and so on.

Old and new enzymes used in textiles

- **Amylase:** desizing.
- **Cellulase:** biopolishing of fabrics and cellulose garments, stone wash of denim garments.
- **Protease:** treatment of protein fibres (silk and wool).
- **Catalase:** elimination of hydrogen peroxide after bleaching.
- **Laccase and peroxidases:** oxidation of dyes.
- **Lipase:** elimination of natural triglycerides (in scouring) or present in desizing (tallow compounds).
- **Pectinase:** bioscouring of raw cotton.

From the end of the eighties till today, the biggest development of modern enzymology was made in the textile segment with the introduction of new cellulase for finishing cellulosic fabrics and garments, of protease for the treatment of wool and silk, of catalase for the elimination of hydrogen peroxide after bleaching, of new amylase types for desizing processes, and of laccase for oxidation of dyes such as indigo.

A new and very interesting application currently being developed is bioscouring raw cotton using alkaline pectinase, as an

alternative to traditional treatments involving caustic soda and high temperatures.

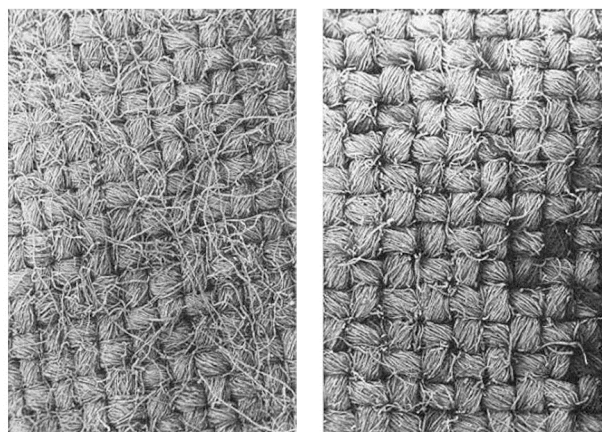
As a large part of fibres processed in the textile industry are of a cellulosic nature (cotton, linen, viscose, Lyocell from wood pulp etc), this segment represents a great opportunity for enzyme treatments. In particular, the uses of cellulase in the textile industry are very varied and in continuous evolution thanks also to the studies carried out in recent years in Italy by Mr Galante and Mr Monteverdi from the Lamberti research centre.

Of the most important results from current research, the following is worthy of mention:

- enzymatic stone wash of denim garments
- biopolishing, meaning superficial defibrillation of fabrics or garments, before or after dyeing;
- removal of the imperfections of immature or "dead" fibre and cotton;
- the modification of hand characteristics and the permanent softening of fabrics;
- improvement of the quality of printing;
- a possible increase in affinity for dyes.

The uses of cellulase in textiles permits the development of a new range of finishing and "fashion effect" industrial processes for fabrics and garments, with an absolutely environment-friendly approach, as it is entirely based on completely biodegradable biological agents, with the following advantages offered by the enzymatic stone wash with cellulase compared to the sole use of pumice stone:

- shorter treatment times;
- minimal damage to machinery;



Picture 157 - Effect of biopolishing: before (left) and after (right) the enzyme treatment.

- increased machine load for every work cycle, with higher productivity in laundering;
- reduction of tearing caused by pumice stones;
- substantial reduction or even elimination of the production of pumice dust, to be disposed of as solid refuse or waste;
- better consistency and reproducibility of stone wash treatment, with also better flexibility of treatments and better final looks obtained;
- less intense manual work in laundering;
- better versatility in using the machine;
- in the case of cellulase liquid formulae, the possibility of using the automatic and computerised dosage systems;
- improved environmental and laundry work conditions.

Biopolishing or biofinishing with cellulase is carried out both on pieces as well as made up garments and it can be compared to an enzymatic “singeing process”, carried out before dyeing or after dyeing also to give a sort of stone wash effect. It is widely used on made up garments, without technological alternative, while on a piece traditional singeing can be used. Nevertheless, in this latter case, that particular soft hand effect typical of cellulase cannot be obtained. Biopolishing treatments permit:

- Elimination of dead or immature cotton, of neps and surface hairiness.
- "Natural" softening with an improvement of hand and drapability.
- Permanent prevention of reiterated fibrillation and pilling.
- Increase in hydrophilic properties, particularly in the case of terry fabrics.
- Better cleanliness and brightness, as well as uniformity of dye.
- Better overall quality of the material.
- The possibility of creating finishings to suit new and original fashion effects.
- Use of an entirely environmentally friendly process.

Enzymatic finishing or surface biopolishing is the result of a combination of enzymatic hydrolysis and mechanical action, whose main factors to consider are:

Mechanical action

- Type, design and management of machinery.
- Process time
- Material load and liquor ratio

Enzymatic action

- Type and quantity of enzyme
- Time, temperature and pH of the process
- Nature and concentration of the chemical auxiliaries present
- Thermal and/or alkaline inactivation of the enzyme at end treatment.

Recent formulae of cellulase and amylase are available, to degrade amide and derivatives of cellulose (such as CMC), and more recently a combination of amylase plus lipase has also been proposed.

There are various scientific developments under way on amylase which could lead to results of a certain interest also for the textile industry, for example:

- Amylase with acid pH, of possible use for desizing in combination with acid extract scouring.
- Amylase with alkaline pH (around 8-9) for desizing in combination with bioscouring with pectinase or however with pH closer to that of bleach.
- Amylase resistant to oxydising condition, capable of being used at the same time as a delicate bleaching process.
- Amylase with activity and stability independent to the presence of calcium ions, which would avoid the addition of calcium chloride in the liquor and would permit the use of stronger chelants or sequestering agents, without risking inactivating the desizing enzymes.

In treating natural fibres composed of proteins, like silk and wool, protease can be used. The latter is composed of a large family of enzymes specific for hydrolysis of proteins, being able to hydrolyse the peptidic link between adjacent amino acids.

A very vast range of protease exists in nature, from every possible source of life (microorganisms, plants, animals) with very diverse properties, different optimal pH levels and temperature, and other biochemical characteristics.

Nevertheless, the sources of industrial protease are by now almost solely microbes obtained by fermentation techniques. Vegetal protease, like papaine and bromelaine, or animal protease like trypsin, chemostrypsin and pepsin, have almost been entirely abandoned for industrial type processes.

Enzymatic degumming of silk using protease permits the sericin to become hydrolysed and at the same time other protein residues deposited by the silkworm.

Compared to traditional degumming of silk using soap in alkaline conditions, enzymatic degumming, if carried out correctly, prevents damage or weakening of the fibre from occurring, obtaining a more uniform coloration, with a less harsh environmental impact compared to surfactants.

Currently, particular protease is used also in the preparation and finishing of silk pieces or articles.

Through this enzymatic treatment, special effects are sought for softening and for the hand (e.g. peach-skin, draping, suede-like effects etc) demanded by fashion or the market.

It should, however, be underlined that, while protease on silk can certainly give interesting and commercially valid results, they are still difficult treatments to carry out correctly in order to avoid irreversible damage.

Possible uses of enzymes:

- 1) Limit the typical tendency of wool to "shrink and felt"
- 2) Solve dimensional stability problems
- 3) Provide "machine wash" characteristics for the fabric
- 4) Eliminate the negative properties emerging in fabric care processes (e.g. hygroscopic expansion)
- 5) Enhance the fabric colouring
- 6) Prevent the pilling effect after some finishing processes
- 7) Eliminate moths (in alternative to the conventional carbonising methods)
- 8) Bleaching of wool
- 9) Wool fabric bioscouring
- 10) Possibility of enhancing the original fineness and softness characteristics of wool
- 11) Enhance the evenness of wool fabric fibres subjected to pre-dyeing treatments
- 12) Obtain stone-wash effects on yarn dyed fabrics, but above all on piece-dyed wool fabrics
- 13) Improve the imbibition properties of wool fabrics
- 14) Possibility of obtaining combined "effects" to ensure flame-retardant or water-repellent properties, etc.

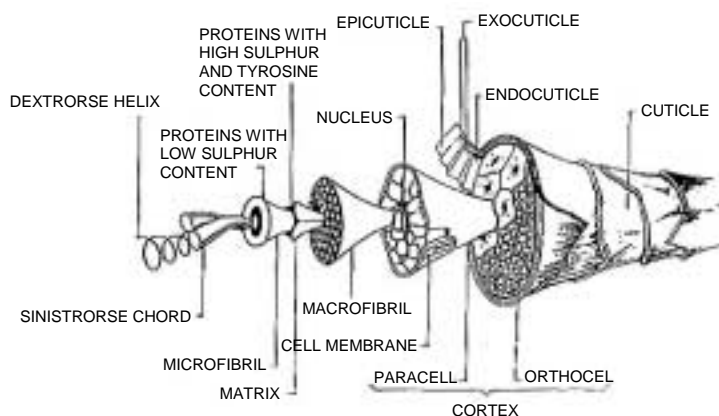
One of the intrinsic properties of wool is its tendency to felt and shrink when wet under conditions of mechanical agitation.

In relation to the various theories proposed to explain this property it is generally accepted that the "differential frictional effect" (DFE) plays a fundamental role in the process. The DFE is correlated to the morphological scale-like structure of the fibres, because of which they can move only in a unidirectional manner towards their roots, but not in an opposite direction, "blocking each other" therefore if subjected to mechanical stress when wet. In practical uses it is extremely convenient to use shrink proof wool, partly due to limitations imposed by dry cleaning and market demand for risk-free home washing of woollen garments.

The techniques used to produce shrink proof wool modify the fibre with rather drastic oxidative treatments, at times followed by applications with cationic resins to preserve the dimensional stability of the wool.

The majority of these processes use chlorine gas, or chlorine or hypochlorite salt. Nevertheless, due to the growing limitations of use of chlorine as an oxidant, there is a growing interest in using more ecological and safer alternatives to produce shrink proof wool.

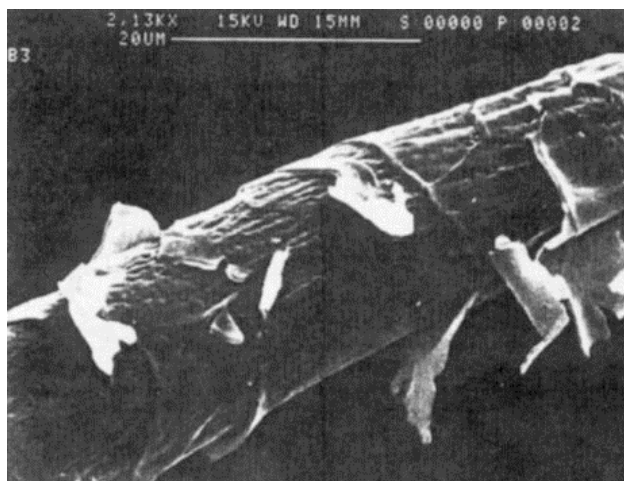
Wool can be considered an almost ideal substrate for many enzymes, like heterase, protease, lipase and other enzymes which break the disulphide bonds of cystins in keratins. The fibres of wool are, in fact, essentially composed of protein and lipids, and are formed by two main morphological structures: the cuticle and the cortex.



Picture 158 - Morphological structure of a wool fibre

The cuticle confers to the fibre the scale-like outer look and it is in turn composed of 75% protein and 25% lipids.

The common anti-felting treatments with chlorine cause to a varying extent a functional modification (resistance to felting) associated with a morphological modification (a marked filing down of the scales of the epicuticle easily seen with a SEM).



Picture 159 - Photograph taken by a SEM which highlights the attacked wool.

On wool, with some protease base enzymatic preparations, interesting effects can be achieved which have some commercial importance, such as:

- Softening and modification of hand characteristics.
- Anti-pilling and surface cleaning.
- Better drapability.
- "Aged" look for garments of clothing.
- Improved comfort.

In the case of anti-pilling treatment for wool woven and knitted fabrics, a protease has been launched on the market which can be used solely on pre-chlorinated wool. Unfortunately, treatments using only protease do not confer anti-felting properties on wool.

In the textile industry, particularly in dyeing, catalysis represents a safe and ecological innovative application for eliminating hydrogen peroxide after the bleaching process and before dyeing. The use of this enzyme instead of more traditional chemical reactants (e.g. reducing alkaline detergents such as hydrosulphite or thiosulphate, magnesium salts etc) permit:

- the avoidance of repeated rinsing cycles, leading to considerable savings in water.
- carrying out of dyeing in the second liquor rinse or even in the first, following corrections of temperature and pH.
- a reduction in process times.
- lower energy requirement.
- the avoidance of polluting chemical effluents.

Recently a new oxidoreducing (laccase) enzyme was also proposed for breaking the irreversible oxidative breaking of indigo which gives denim garments a "cleaned" effect on backstaining (using low quantities) or bleaching (using higher quantities).

Finally, a new process for the bioscouring of raw cotton was presented for the first time in Italy. The bioscouring of raw cotton as an alternative to alkaline scouring has been studied in depth over recent years. The basic idea is simply that of hydrolysing using enzymes those non-cellulosic components responsible for water repellency of cotton, using a specific degradation process in delicate pH and temperature conditions, then removing them with a successive hot rinse.

The enzymatic process are very specific and can therefore be direct only towards components which need to be removed, maintaining the cellulose intact, with therefore a lesser loss of weight and resistance to fibre, a lower COD and BOD in plant wastewater.

Considering the composition of the entire cellulose fibre, pectin, protein, wax and hemicellulose, various families of hydrolytic enzymes have been evaluated in bioscouring, used individually or in combination, such as: cellulase, pectinase, protease, hemicellulase, and lipase.

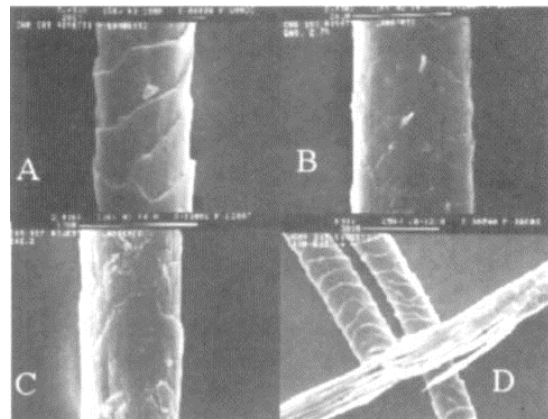
From many studies published or presented at scientific symposiums it has emerged that a treatment with pectinase followed by a hot rinse is able to confer hydrophilic properties on cotton and make cotton absorbent as well as being a chemical scouring process.

On the contrary, protease, hemicellulase and lipase do not seem to offer positive effects, while cellulase can weaken the fibre. This result is explained by the facts that:

- Waxy material, pectic substances and proteins from the cuticle and primary wall are associated and present in an amorphous state.
- The primary wall has higher amorphous properties than the secondary one.
- The external surface of the fibre can therefore be hydrolysed more easily than its core.

The pectinase destroys the structure of the cuticle, hydrolysing the pectins and removing the links with wax and protein, as well as between these and the remaining fibre structure. The pectin links the wax to the cellulose of the primary wall, but it is not necessary to eliminate all the pectin for providing hydrophilic properties. Even when 30% of the residual pectin remains on the fabric, a wash at 80-90°C after a dwelling stage eliminates the solubilised waxes.

This pectinase is to be more exact, a lyase pectin, it acts therefore on the pectin independently to its degree of methoxidation. Bioscouring is applied on woven fabrics in continuous processes and on knitted fabrics in batch processes. It can be applied with an exhaust process or by impregnation (pad batch) in a special buffer at pH 8-9 containing an imbibition agent, at a temperature of between 50 and 60 °C or lower and for variable times from some tens of minutes to some hours, depending on the fabric, the quantity and the dwelling temperature. In these conditions, it is also possible to combine the two treatments of scouring and desizing into just one operation, the conditions of use of pectinase and amylase being compatible. A hot rinse follows to eliminate the hydrolysed components and freed waxes. The efficiency of the bioscouring is measured mainly by the hydrophilic properties of the fabric treated. The same degree of hydrophilic properties are obtained with the drop test, comparable to chemical and enzymatic scouring.



*Picture 160 – Protease treatment of wool
A: non-treated wool; B: wool treated with specific products; C: wool treated with protease; D: wool damaged by protease.*

The residual content of pectin is comparable in the two approaches, but it is not influential on the hydrophilic property, this being determined mainly by waxy components on the cuticle. On the other hand, with bioscouring alone, the moles are not eliminated (in fact it is a wooden material) and it does not increase the degree of white.

Both these aspects are however resolved in the successive bleaching.

Of the potential application and commercial advantages of the bioscouring, the following are worthy of note:

- Saving of water and energy.
- Lower environmental impact and easier to treat wastewater.
- Better compatibility with other processes, machinery and materials.
- Lesser attacks on the fibre structure, loss of weight and resistance, with improved quality of the article.
- Improved hand characteristics.
- Possibility (still to be proven) of a higher degree of polymerisation of the cellulose and a lesser tendency of the fabric or fibrillation later pilling phenomena.
- Better and more uniform affinity for dyes.
- In the case of woven fabrics, the possibility to combine the two desizing and bioscouring steps in just one; in the case of knitted fabrics, combining bioscouring with biopolishing using cellulase, with a jet or overflow machine.
- Possibility of scouring cotton even when blended with more delicate fibres.

Bioscouring is therefore only in its infant stage as a proposal for large scale industrial application on woven and knitted fabrics as well as on yarns.

Laboratory figures and pilot tests are without a doubt encouraging, but it remains to be tested in an installation to say how valid and competitive this new textile enzymology process can be.

Until ten years ago, the use of normal amylase for desizing was more or less the only noted application and it would have been difficult to imagine such a boom in the development of new enzymes and their relative applications in the textile field.

There is still a lot of progress to be made, such as:

- costs must become more competitive;
- the ease of use and parameter control must be improved;
- the question of inserting enzymatic treatments stages in continuous processes;
- new enzymes must be developed, above all active in a wider range of pH environments and temperatures;
- rapid, simple and economic methods of enzymatic activity must be developed to offer the operator better control over the process.

Enzymology is however finding increasingly large space in the practice of preparing and finishing textiles. It is not a technology which eliminates either chemicals or textile machines, but it integrates well with these.

For a textile industry like the one in Italy, dependent for its commercial success above all on an excellent capacity and sensitivity to finishing textile goods, as recognised throughout the world, a good ability in enzymology becomes therefore an excellent factor linked to competitive advantage.

The Influence of Finishing Treatments on Dyed Goods

The purpose of finishing treatments is to give cellulose articles and relative blends with synthetic fibres determined properties that are advantageous in terms of use. Nevertheless, we must add straight away that these treatments also cause undesired effects under a double aspect: mechanical-technological (e.g. reduction of strength) or appearance (e.g. colour change and influence on the solidity of tones).

Here we above all discuss the influence that finishing treatments can have on dyeing and prints, though only in general terms as in many cases the problem is linked not only to the type, but also to the quantity of cross-linking agent as well as the method of application and the composition of the overall recipe, which also includes catalysts and additives. It must also be remembered that it is impossible to establish regulations on this subject to generalise dyes by class or certain assortment. Therefore even the following information, which is based on experience gained and the results of many research projects, is only indicative: we therefore recommend that the finisher, for safety reasons, carries out trials under normal working conditions.

The influences of finishing on dyed goods are described in the example of cellulose fibre, but they are suitably adequate even for relative blends with synthetic fibres.

Influence on colour

Dye and print colour can be more or less strongly influenced by finishing treatments, with the possibility that variations in both tone and intensity occur.

Individual dyes as well as finishing products and conditions are responsible for this. The individual cross linking agents on their own are of secondary importance for colour change, meaning that they cause a variance in tone practically the same as the dye itself in most cases, and under similar conditions. On the other hand, the influence of catalysts is entirely different.

The most favourable results are obtained using zinc chloride or magnesium chloride.

Zinc nitrate compromises the tone only in some cases, while ammonium chloride as well as organic hydrochlorides (e.g. 2-amino-2-methylpropanol-hydrochloride) can cause a sharper colour change.

Additives and the conditions of condensation have generally less importance in this regard, nevertheless even these factors should not be entirely overlooked.

Data relating to the influence of the dyes on finishing, often reported on relative colour cards, provides a reference, but does not permit definitive conclusions to be drawn.

It is necessary, in fact, to consider that the environmental conditions of the various finishing mills makes a large number of variants possible, which cannot all be born in consideration on one colour card.

To operate safely, it is therefore necessary that the finisher experiments in his own laboratory to verify which dyes and finishes are suitable for the particular conditions. Naturally, the company who produces the dyes as well as finishing products will always be willing to elaborate on ideal proposals for users.

Even though changes in colour are observed especially when we are dealing with substantive dyes, preliminary trials are also required for reactive dyes as well as for vat dyes (which are less susceptible to the changes in question), in order for the maximum work safety in the mill to be observed.

The trials should also contemplate the dyes that are used for the dyeing of synthetic fibre (e.g. polyester) in blends with cellulose fibre.

Metamerism

By metamerism is intended that phenomenon which causes two objects to present the same colour when they undergo a series of observation conditions, different colours on the other hand under a different set of conditions. In particular, with exposure to light certain dyes present the phenomenon of metamerism, such as some yellow vat dyes. This characteristic is a property of the dye, which cannot be influenced in a positive sense, but it can be accentuated by finishing. Even catalysts highlight the metamerism property of some sensitive dyes and for this reason ammonium salts are strongly advised against, they should be replaced with zinc salts or magnesium chloride.

It is therefore a good idea to try and resolve the problem of metamerism dyes using which are as insensitive as possible for dyeing or printing.

Influence on fastness to light

Fastness to light of dyeing or printing with reactive or direct dyes can reduce in a more or less significant manner the finishing treatment.

In general, the vat dyes are practically uninfluenced with some exceptions, including some leuco-esters which should however always be subject to prior checks.

Given, however, that in practice determining fastness to light implies that time is widely available, it is recommended to use dyes with a high level of this fastness as far as possible as well as finishing products which could affect it only in a very slight way.

Comparing various finishing treatments on dyed goods, it is noted that individual cross linking agents exercise a differentiated influence on fastness to light, even when they are applied without catalysts on dyed goods, that is therefore where a reaction cannot occur. It can be concluded that the catalyst has more or less no influence on fastness to light.

Influence on fastness to rubbing

Fastness to rubbing is affected by determined products mainly in the case of textiles (polyester, acetate) dyed with dispersion dyes.

Of these products, we cite those of preparation for weaving, with winding oils, softeners, and water repellent agents.

Often such a reaction results evident only after a lengthy storage of the dyed goods. Generally, the solidity to rubbing is not influenced by cross-linking agents and catalysts.

Sometimes an abrasion of the fibre is erroneously mistaken for bad solidity to rubbing.

This inconvenience is on the other hand due to an accumulation of finishing products, which can provoke a certain brittleness of the cellulose fibres on the surface of the fabric. To avoid this problem as far as possible, the following should be observed:

- carry out singeing operations with great accuracy, eliminating hairiness;
- avoid bleaching errors, which would provoke deterioration of the fibre;
- use optimal quantities of cross linking agents; in such a way as to avoid provoking excessive brittleness of the fibre
- keep to ideal conditions for drying after the application of finish and avoid the operation being carried out too quickly