Mercerizing with Ammonia

Even if the textile world remains hesitating because it is not really familiarized with the problems of the use of ammonia, these are now mastered thanks to the collaboration between ammonia producer and textile finishers. It may be seen further in this paper why the use of ammonia in textile finishing may be considered as ideally ecological.

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Although research reports concerning the action of ammonia on cellulose may be found since 1861, truly scientific results were only achieved in that field between 1926 and 1937.

Research with liquid ammonia in fact began with Bernardy (1925), who found that the action of ammonia on cellulose was much weaker than that of concentrated solutions of caustic soda and that fibre characteristics were, in the two cases, completely different. He observed, on the other side, an increase of the volume of the cellulose, but no direct attack by liquid ammonia, as in the case of a caustic soda treatment.

Some decades had to pass until these results found around 1967 an industrial application. First they were applied to the treatment of cotton yarns, later to the treatment of woven and knitted goods.

The industrial exploitation of the procedure began effectively in the EC a decade ago: in Germany on woven goods (the company Martini in Augsburg) and in Belgium for both woven and knitted goods (the company Veramtex in Brussels), the latter being the only company in the world able to treat both kinds of fabrics.

What is ammonia?

To the contrary to what may be believed, ammonia is a natural substance. With the chemical formula NH_3 (one nitrogen atom and three hydrogen atoms), the ammonia is the unavoidable intermediate in the biological processes since the origin of life.

In fact, with the exception of some leguminous plants, plants and animals are unable to fix nitrogen out of the air to elaborate proteins, the essential elements of living beings. Ammonia and its derivatives are the sole sources of assimilable nitrogene they have at their disposal.

Ammonia is naturally present in decomposed waste of animals and plants valorized in agriculture.

As the available quantities are far from being sufficient to secure the worldwide alimentary needs, an important industry has developed to supply the agriculture with the ammonia and its derivatives it needs. Large amounts are also being used to produce synthetic fibres like nylon and acrylics.

At ambient temperature and atmospheric pressure, ammonia is a gas with an irritating characteristic smell. It is extremely well soluble in water, forming the "ammonia" solution well known to housewives.

Liquid ammonia is now produced worldwide in hundreds of plants with a capacity of 800 to 2'000 t per day each.

Fig. 1: Installation for ammonia treatment on woven and knitted goods   Picture: Veramtex

The Veramtex process

The treatment is being made continuously with lengthwise tension. It consists in an impregnation of the goods with liquid ammonia (NH3) at atmospheric pressure (i.e. at boiling temperature of –33 °C), followed by the elimination of the reagent by evaporation (Sanforset process) or by rinsing with water (Veramtex process). The cellulose is treated under tension in presence of an alkali, which means mercerizing by definition.

Like mercerizing with caustic soda (NaOH), ammonia produces changes in the structure of cellulose – reorganisation of the crystalline network with cellulosic chains rotating and translating around their axle – giving a better accessible network to reagents.

The small dimension of the ammonia molecule and the weak surface tension of liquid ammonia favour the penetration of the alkali into the fibre core, without destroying the microfibrils, as it may be observed with other swelling agents.

The ammonia which has penetrated into the fibre is removed very quickly and totally because of its high volatility and extreme solubility in water.

Table I: Results of the ammonia treatment on a 100 % cotton fabric for professional clothings, 290 g/m²

	Sample 1	Sample 2	Sample 3	Sample 4
Tensile strength				
Warp	1191.9 N	1267.5 N	1393 N	896.6 N
Weft	890.7 N	864.3 N	879 N	662.2 N
Elasticity				
Warp	16.30 %	10.20 %	11.20 %	12.40 %
Weft	11.10 %	15.60 %	20.80%	13.80 %
Tear strength				
Warp	50.2 N	29.3 N	30.8 N	48.3 N
Weft	48.1 N	24.0 N	28.2 N	40.2 N
Creasing angle				
Dry		183.6°	193.2°	220°
Wet		128.8°	143.0°	235°
Creasing angle (3'000 rpm/90 s)		4.40 %	3.60 %	3.90 %

Sample 1 Gray fabric
Sample 2 Bleached sample
Sample 3 Bleached + NH3
Sample 4 Bleached + NH3 + resin

Differences in the process

Penetration of ammonia into the fibre and its elimination are nearly instantaneous. Thus the treatment is fast and the mercerizing line short (impregnation and evaporation time between 15 and 25 s).

The use of a reagent at its boiling temperature stabilizes de facto the function characteristics such as temperature, concentration, tension and avoids the addition of auxiliaries.

Mercerizing with ammonia allows to recover almost totally the alkali and its reuse continuously through a purifying distillation, operation which is almost impossible with caustic soda which remains polluted, especially when mercerizing gray fabrics.

As the remove of ammonia is very quick, water consumption is reduced by more than a half.

The penetration of the reagent into the fibre core and the elimination of the function characteristics result in constant and reproducible effects.

In conclusion, the process:
- operates with a natural substance like ammonia,
- results after the treatment in reagent free textile goods,
- does not produce polluting waste neither in a gas nor in a liquid form, the ammonia used is entirely recovered, purified by distillation and recycled in the installation with a yield of nearly 100 %.

Differences on the fibre

The properties provided by traditional mercerizing with caustic soda are more or less preserved with ammonia, i.e. increase of the affinity to dyestuffs and change in the appearence. But the behaviour of ammonia with the cellulose differentiates from the behaviour of caustic soda in the following manner:

Ammonia, a weak alkali, does not damage the fibre contrary to the very aggressive caustic soda; mechanical properties are increased (abrasion resistance, tensile and tearing strength); touch remains pleasant even after many washings;

Ammonia swells less the fibre which will behave in a more plastic and more malleable manner against solicitations by wearing and washing. The article life is increased and the appearance as new is maintained for a longer time. The difference in swelling explains also the more brilliant aspect of the fibre after the caustic soda treatment and the satin gloss after the ammonia treatment;

Caustic soda does not penetrate to the fibre core as does the ammonia; this results in very even and uniform goods, with very efficient decreasing properties. The gradual shrinking after washing is almost stopped and colours do not change;

Drying after later operations will be quicker. In fact, the "architecture" of the micropores created by the small molecule of ammonia facilitates transfer and elimination of the water and the aqueous solutions contained in the cotton during centrifugal or mechanical removal of water.

Valorization of the effects

Mercerizing with ammonia modifies the cellulose morphology and changes considerably the properties of the cotton fibre because, together with the increase of affinity to dyestuffs, it increases also the affinity and the sensitiveness to all other chemicals and finishing treatments. Thus, finishing treatments have to be adapted to the new characteristics. Doing so, a remarkable synergy between the ammonia treatment and the finishing is realized.

Woven goods

Before treatment, the goods have to be desized, kier-boiled and bleached (without an optical brightener) carefully. After the ammonia treatment, it is not recommended to submit the goods to another strong alkali treatment.

On the other hand, a slight residual alkalinity may prevent, by partial inactivation of the catalyst, an optimum reticulation when applying a finishing resin. Thus the goods should be neutralized before that operation.

According to the article and its destination, as well as to the required properties, the goods will be submitted to a dry condensation, a damp or a wet reticulation.

For example, the ammonia treatment on a poplin, coupled with a damp reticulation, results in a usage/resistance relation which was considered to be an ideal goal during decades without being reached (a German shirt-maker certifies that his 100% cotton articles, treated as mentioned above, need not to be ironed after washing and drying on a coat-hanger).

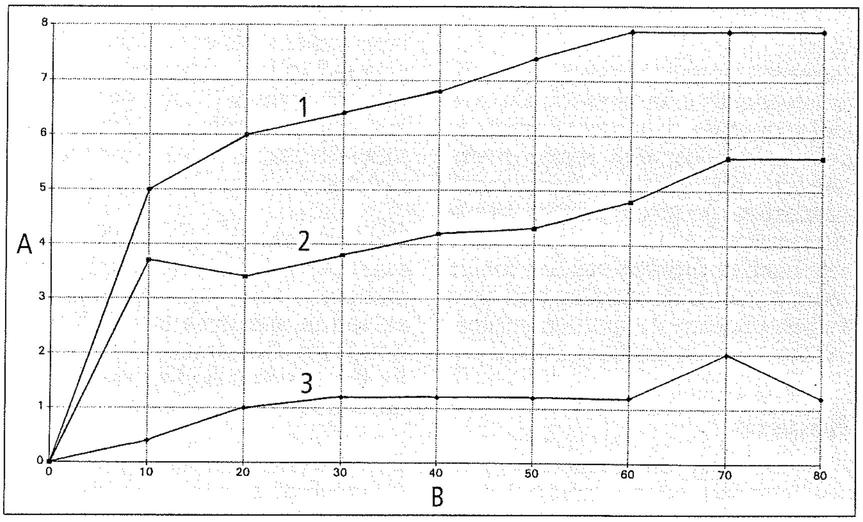

Fig. 3: Shrinkage after multiple washings; cotton fabric for professional clothings, 290 g/m²
A Shrinkage in length in %
B Number of washings
1 Bleached
2 Bleached + NH3
3 Bleached + NH3 + resin

The main improvements

The main improvements are:

- increase of the dry and wet creasing angle *(tab. I)*;
- a better wash-and-wear behaviour;
- increased resistances in most cases (tensile strength, tear strength, abrasion) *(tab. II)*
- a nice touch
- long-lasting stability (progressive shrinkage is considerably reduced) *(fig. 3)*

Concerning professional clothing, numerous weavers have opted for 100 % cotton treated with ammonia, obtaining the same results as with polyester/cotton, the latter being however less comfortable, less absorbent particularly for perspiration, becoming translucent when used and not being biodegradable.

After the ammonia treatment on bast fibres, results are even more spectacular *(tab. II)*.

Knitted good

The above-mentioned recommendations are less imperative on knitgoods, as the required properties are generally not the same as for woven goods (resistance, anti-crease).

The goods are mercerized in gray or yarn dyed stage (apart from naphthols, all dyestuffs are resistant to ammonia). Finishing is not much different from the convention-

Table II: Mechanical properties of a 100 % linen fabric for garments

	Convent. finishing	Finishing with dry condensation		Convent. finishing	Finishing with damp reticulation	
		without NH_3	with NH_3		without NH_3	with NH_3
Shrinkage after 5 washings at 40 °C						
Warp	−8 %	−3.50 %	−1.10 %	−8 %	−4.20 %	−1.20 %
Weft	−8 %	−3.50 %	−2.00 %	−8 %	−4.00 %	−1.50 %
Creasing angle (warp + weft)						
Dry	127 °	170 °	250 °	127 °	145 °	240 °
Wet	124 °	165 °	235 °	124 °	170 °	255 °
Wash-and-Wear behaviour (Monsanto)	1.5	3	4.3	1.5	3.5	4.5
Abrasion resistance (Accelerator 3'000 rpm/120')	−10 %	−32 %	−16 %	−10 %	−26 %	−10.50 %

al finishing as long as no resin is used.
However, as mercerizing with ammonia results in increased mechanical properties, it is now possible to treat knitgoods with resins maintaining acceptable mechanical properties (tensile strength, bursting resistance).
The main improvements are: touch, elasticity, durable stability, anti-twist and mechanical properties improving the yield in garment-making.

Prospects

Products with unequalled properties, comfort, touch, non-polluting process using less water, possibility to substitute PES/CO by 100% cotton, these are the trumps which explain the increasing success in Europe, mainly in Germany, in Switzerland and in Austria.

It has been proven that liquid ammonia can be applied and recycled reliably in the textile industry. Environmental constraints becoming more and more strict, it may be envisaged to use ammonia as a solvent for dyeing. Continuous dyeing with liquid ammonia is known. Ammonia replaces water to bring the dyestuff onto the fibre.

The process is astonishingly simple. The woven or knitted goods are mangled with the dyestuff dissolved in ammonia at –33 °C. The goods are then steamed in order to fix the dyestuff and to remove the ammonia.

The following washing, to eliminate the dyestuff in excess on the fibre, completes the dyeing cycle.Ammonia being a remarkable solvent, the dyestuffs are dissolved monomolecularly.

All the classical dyestuffs tested up to now are dissolved in ammonia, and, apart from acetate, all fibres may be dyed according to that process.

It is a process which avoids all the problems in relation to the quality of the water. It is not necessary to control the pH or the temperature of the dyebath as all parameters remain constant by the nature of ammonia.

On the other hand a lot of auxiliaries and chemicals are withdrawn, i.e. salt, carriers, wetting, sequestring, retarding or levelling agents.

Trials have brought to evidence the good penetration of the dyestuffs, a short steaming time related to the type and the contexture of the goods (from 3 to 30 s) and an excellent levelness of dyeings.

That technology differentiates from the new dyeing process with supercritical CO_2 (which binds to a discontinuous dyeing in pressure vessels resistant to 74 bars) by its simplicity and the possibility to mercerize and to dye simultaneously all cellulosic fibres. ■