Water-Repellent Finishes

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AT the very outset, it is necessary to distinguish between "waterproof" and "water-repellent" textile surfaces. A waterproof fabric is one in which the pores of the fabric are filled with appropriate substances, and the fabric shows very little air permeability. A water-repellent fabric, on the other hand, is one in which the fibres are usually coated with a hydrophobic compound and whose pores are not filled in the course of the treatment. The latter type of fabrics, however, are quite permeable to air and water vapour.

The tendency of a solid to resist wetting depends on the chemical nature, roughness and porosity of the surface and on the presence of other molecules on the surface.

When a drop of water is placed on a solid, it forms an angle of contact with the surface. When the angle of contact is less than 90°, the surface is said to be wettable, and when the angle is larger, the surface is said to be non-wettable. The angle of contact is determined by the factors given above.

Principle of water-repellent finishes depends on the chemical nature of the surface and on the presence of other molecules on the surface of the fabric. Before imparting a water-repellent finish to a fabric, the following points should be considered.

Firstly, the fabric must be properly prepared to accept water-resistant treatments. The fibre surfaces must be free from impurities. It is a common practice to test the pH and absorbency of the fabric.

The second factor is the choice of the proper water-repellent material. Compounds used in imparting water-repellent finishes to textile fabrics show a selective action i.e. a certain compound suitable for cotton fabric need not be suitable for, say, viscose fabric.

The third factor concerns the actual application of the water-repellent material to the fabric. In preparing the bath, the manufacturer's instructions must be followed. Regardless of the type of compound used, optimum results can only be obtained when complete penetration of the fabric is effected by the water-repellent material. This is easily achieved by the use of a three-bowl padder, or by passing the goods through a two to four dip immersion box in front of the padder. A heavy nip is also preferred as it aids in driving the water-repellent material into the fabric between individual fibres. Drying conditions and subsequent operations are governed by the type of compound applied.

Water-repellent finishes may be broadly classified into two types as : (a) those in which the fabric is covered with a hydrophobic substance such as wax and (b) the fibre itself is made hydrophobic or water-repellent by chemical combination with long chain compounds.

In the first type, the object of the water-repellent treatment is to coat each and every individual fibre with a continuous hydrophobic film, without bonding the fibres to each other, or in other words forming a film over the interstices of the fabric. To perform the operation effectively, the film-forming substance must be tough, pliable and elastic and

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must adhere tenaciously to the fibre surface. The types of compounds used are:

(1) Aluminium compounds, alone or with soap.
(2) Zirconium compounds.
(3) Oils, fats and waxes.
(4) Vegetable and animal proteins.
(5) Synthetic compounds of high molecular weight.
(6) Silicon compounds.

(1) *Aluminium compounds:* The use of aluminium acetate formed one of the earliest processes for obtaining water-repellent finishes, in which insoluble basic aluminium acetate remained in the fibre. A later development in which use is made of aluminium soap, has continued upto the present day and is usually a two-bath process. It may, however, be carried out as a one-bath process by impregnating the cloth with a dispersion of aluminium soap in water, the dispersing agent being a protective colloid, such as glue, soap, etc. In another one-bath process, the cloth is padded through a solution of aluminium soap in an organic solvent. The aluminium finish is the cheapest type of water-repellent finish, but it is not very durable.

(2) *Zirconium compounds:* Water-repellent finishes may also be obtained by using zirconium compounds. They can be applied by various processes such as: (a) treatment with a solution of zirconium oxychloride, buffered with aluminium acetate, followed by drying, (b) padding in a wax emulsion, followed by a treatment with oxychloride solution, (c) impregnating with a double carbonate of zirconium and soap, followed by heating to precipitate a zirconyl monofatty acid compound, and (d) processing in an aqueous emulsion of waxes containing zirconium salts in the water phase. This class of compounds has attained considerable importance in Germany and U.S.A. The treatment is particularly effective on the synthetic fibre fabrics and regenerated cellulose rayons. This type of finish is intermediate in cost and performance between the durable wax treatments and the renewable aluminium treatments.

(3) *Oils, fats and waxes:* Showerproofing with wax in various forms has been applied to many lightweight dress materials, sometimes in conjunction with aluminium acetate.

Good quality paraffin wax (M.P. 57°C.) may be employed alone or in conjunction with a softening agent. The wax may be applied in various ways, such as from solution, by friction and by spraying in a molten condition or from an aqueous emulsion. The emulsion method is perhaps the commonest method of shower-proofing fabric with wax, and many commercial emulsions are available. An important property of cloth treated with these emulsions is that their finish differs only very slightly from that of the original material.

An important advance in emulsification process has been made by Du Pont. It depends on the use of salts of partially de-acetylated chitin in conjunction with paraffin wax and a fixing agent, such as aluminium acetate. The water repellency thus obtained is much superior to that obtained by the older methods.

(4) *Protein products:* Numerous processes have appeared utilising protein substances such as glue, gelatin and casein. They all depend on the fact that these products are rendered insoluble by the action of bichromates, formaldehyde, tannin or aluminium compounds. A number of protein products are marketted today under various trade names, such as Mystolene of the Catomance Company, etc. These can be applied to animal and vegetable fibres. Mystolene filler is a protein-aluminium complex in the form of an emulsion which is applied to the fabric after suitable dilution.

(5) *Synthetic compounds:* Synthetic compounds of high molecular weight have been used as water-repellents. This is an almost inevitable outcome of their application in other branches of textile finishing.

A recent development in Germany is the development of Persistol VS, which is stated to attract dirt less readily than most products. Persistol VS is octadecyl-ethylene-urea in a dispersed form. It is used in concentrations of 5%. After impregnation the goods are squeezed and dried at a temperature above 80°C when the reaction is supposed to take place with the fibre.

(6) *Silicon compounds:* Silicones are the latest entrants in the water-repellent finish field. As a class, the silicones seem to be more effective on synthetic fibres. Of late, silicone oil emulsions have been introduced.

It has been found that a superior water-repellent finish can be obtained by immersing textiles in a lower alkyl (methyl-, ethyl-, or propyl-) substituted dichloro-silane or dibromo-silane.

Hydrophobic Fibres: The greater part of textile material which is required to be non-wetting is cellulosic, so that chemical reactions which aim at the production of hydrophobic fibres must be based chiefly on cellulose chemistry.

The two great classes of cellulose derivatives are the esters and the ethers; the former are susceptible to alkali, but the latter class is affected by acids only under conditions that degrade cellulose. Hence, these finishes may be regarded as permanent. Fatty compounds have been used to esterify and etherify cellulose for water-repellent effect.

Esterification: In most cases the acid chlorides are used to bring about esterification. Esters of chlorocarbonic acid (containing C_{16} or C_{18}) combine with cellulose and give water-repellent finishes.

$$\text{Cell—OH} + \text{ClCOOC}_{18}\text{H}_{35} \longrightarrow \text{Cell—O—COOC}_{18}\text{H}_{35} + \text{HCl}$$

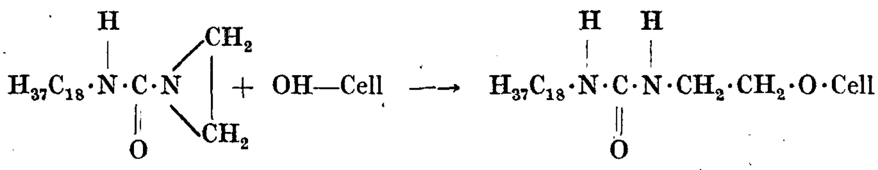
Isocynates may also be utilised in the production of cellulose esters of carbonic acids. Thus,

$$\text{Cell—OH} + \text{C}{\overset{\text{N—C}_{17}\text{H}_{35}}{\underset{\text{O}}{\lessgtr}}} \longrightarrow \text{Cell—O—C}{\overset{\text{NH}\cdot\text{C}_{17}\text{H}_{35}}{\underset{\text{O}}{\lessgtr}}}$$

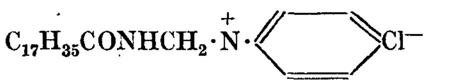
The use of ketenes of high molecular weight represents yet another method of esterification to produce hydrophobic fibres on account of the chemical fixation of a fatty radical.

Etherification: Cellulose ethers of a special type have been found to possess remarkable water-repellent properties, and as the ethers, as a class, are stable to alkali, the new hydrophobic finish is permanent.

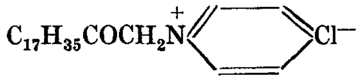
During the World War II, a durable water-repellent finish was developed in Germany by the I.G. Farbenindustrie which was claimed to give excellent results. The process consisted of treating a fabric with N-octadecyl-N-ethylene urea. This compound was claimed to be sufficiently reactive to combine directly with cellulose:



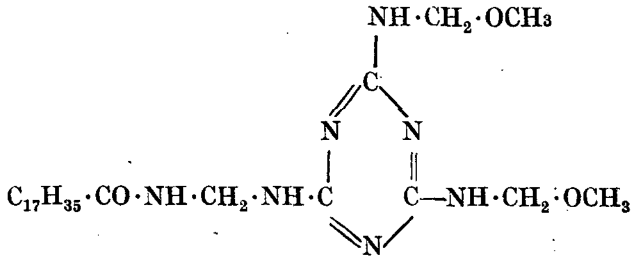
Very durable finishes are obtained by using highly insoluble stearic acid derivatives, such as methylol stearamide, suitably solubilised or dispersed. Velan PF (or Zelan), Norane, Parmel belong to this class. The probable structures are:



Zelan (Du Pont)



Norane (Warwick)

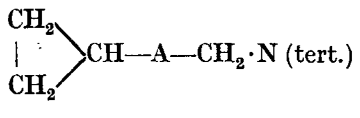


Parmel (Cyanamide)

On heating, the tertiary amine is liberated and we get, $C_{17}H_{35}CONHCH_2$-O-Cell.

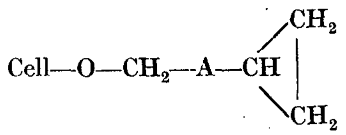
The Velan treatment is divided into three steps—impregnation, drying and heating. The impregnation may be carried out in a jig, winch or padding mangle. The drying may be conducted on drying cylinders, festoon drier or hot-air-stenter. Heating is the most important part of the treatment and should be carried out in a hot-air chamber. The goods must be heated uniformly to the required temperature for a period long enough to give the required effect and the period of heating varies inversely as the temperature.

The standard water-repellent agents mentioned above of the Velan (Zelan) type, which apparently react with fibre molecules, have one reactive functional group only. In contrast, we may have two unlike functional groups, both of which react with the molecule of the fibre. One of them is the quarternary ammonium group as used in Zelan and similar methods; the other is a cyclo-propane group. These compounds have the following general formula:



wherein 'A' generally is a hydrocarbon chain (not over 30C).

Above 100°C tertiary amine is liberated as in Zelan reaction, giving the following:



but the free radical will further decompose, if the cyclo-propane ring opens and reacts with another cellulose molecule to form cross-linkages of the type:

Cell–O–CH_2–CH_2–CH_2–A–CH_2–O–Cell

Such type of compounds impart a very durable water-repellent finish.

A lot of research work on the water-repellent finishes is still going on in the textile laboratories, especially in the U.S.A. and though we have been unable to obtain perfect water-repellency, we are at least slowly approaching the optimum.

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