

Passive and active protection of cotton textiles

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Samenvatting

Bij het rotvrij maken van katoen kan men onderscheid maken tussen passieve en actieve bescherming. Bij passieve bescherming wordt de structuur van de katoenvezel zodanig gemodificeerd, dat de vezel onaantastbaar wordt voor micro-organismen. Deze modificatie kan worden gerealiseerd op microscopisch, submicroscopisch of moleculair niveau. Bij actieve bescherming wordt het weefsel geïmpregneerd met verbindingen, die min of meer toxisch zijn voor het binnendringende organisme.

Een aantal methoden wordt besproken, waarvan enkele in het Centraal Laboratorium TNO werden ontwikkeld.

Het verschil tussen actieve en passieve bescherming wordt geïllustreerd met een laboratoriumexperiment waarbij cellulase-extracten worden gebruikt en met de resultaten van een praktijkproef met legertenten. De merites van het rotvrij maken in het algemeen worden besproken, vooral in verband met de Nederlandse textielproductie.

Introduction

Cotton fibres consist of almost pure cellulose, the most widely spread building-stone in nature. Each year, billions of tons of cellulose are produced on earth. The total amount of cellulose is, however, kept stationary mainly by the action of bacteria and fungi. These micro-organisms produce cellulase, an enzyme which catalyzes the breakdown of cellulose into small molecules, digestible for these organisms.

Beside this useful function of micro-organisms in destroying excess of cellulose, much harm is done to the technical products which man makes from cellulose-containing natural materials. Thus, in the case of cotton fibres, it is necessary to protect them from biological attack. Now practice has taught us that the best way to do this is to keep the cotton materials away from moisture. All of us have been confronted with the stains which occur in a cotton fabric when it is stored in a moist condition. A sufficiently dry fabric will not be damaged. As often the presence of moisture cannot be excluded, many attempts have been made to render cotton fabrics rotproof by chemical means.

Many processes have been worked out, but the number of processes used in practice, is limited. In the following a few processes will be discussed. A classification will be made in: "passive" and "active" treatments. The importance of this classification will be illustrated with some practical experiments.

Passive protection of cotton textiles

In passive protection, the structure of the fibre is modified in such a way that the fibre can no longer be attacked. This modification of structure can

Summary

In rotproofing of cotton a distinction is made between passive and active protection. In passive protection, the structure of the cotton fibre is modified in such a way that the fibre can no longer be attacked. This modification of structure can be effected on different levels: microscopical, sub-microscopical and molecular. In active protection, the fabric is impregnated with compounds that are more or less toxic to the invading micro-organisms. A number of methods are discussed, including some methods developed by the Central Laboratory TNO.

The difference between active and passive protection is illustrated through a laboratory experiment, using cellulase extracts, and with the results of a large outdoor exposure of treated fabrics. The merits of rotproofing in general are discussed, especially in connection with the Dutch textile production.

be effected on a microscopical, a sub-microscopical, and a molecular level. Thus by coating a cotton fibre with a suitable compound, e.g. a polymer, a physical barrier is constructed which prevents a contact between the fibre and the invading organism. Practice has taught us, however, that it is difficult to surround each fibre of a cotton fabric with a faultless coating; always holes and crevices will remain, which then become the gateways for the organisms. Moreover the "handle" of a fabric is easily damaged by coating with polymers, the fabric becoming stiff and boardy.

Another example of passive protection of cotton fabrics is a process in which physical barriers are created on a *sub-microscopical* level. Recent microscopical investigations of the attack of fungi on cotton fibres, also in our laboratory show that attack usually starts in the pores and crevices which are always present in the fibre. When we are able to fill in those pores and accessible places, the attack of micro-organisms can likewise be prevented. Two processes which are more or less based on this principle will now be discussed. The first has been developed in the U.S.A. and is usually called the "acid-colloid-process" [1]. Starting from a solution of melamin-formaldehyde and formic acid in water, a rather stable colloidal solution of partly polymerized melamin resin is formed. This solution is applied to a cotton fabric by the usual impregnation techniques. After drying the fabric is cured at an elevated temperature, e.g. 5 min. at 140°C, when an insoluble resin is formed in the inside of the fibre.

A second process, which also uses melamine-formaldehyde resins, is the "Arigal-C" process, devel-

Table 1

Rot resistance of print cloth finished with trimethylolmelamine acid colloid and other compounds.

Fabric finish	Strength retained after soil burial, %						
	3wk.	6 wk.	9 wk.	12 wk.	15 wk.	18 wk.	21 wk.
Acid colloid, 12% resin add-on	100	100	100	100	100	100	100
Arigal treated	100	93	100	100	100	100	100
Partially acetylated, 22% acetyl	93	93	94	96	94	98	91
Fully acetylated, 35% acetyl	99	97	100	100	98	100	100
Cyanoethylated, 4.0% N	97	90	93	94	98	94	92

Table 2

Influence of „Arigal-C” treatment on fabric properties.

Finish	Resin add-on, %	Breaking strength, warp, lb.	Elmen-dorf tear, warp, lb.	Stoll Abrader	
				Abrasion, flex	Wear cycles, flat
Acid colloid	12	32.53	1.04	87	94
Acid colloid	9	31.18	1.25	67	67
Acid colloid	7	33.44	1.32	96	96
Acid colloid	4	34.32	1.42	184	73
Acid colloid	2	35.14	1.60	499	85
Conventional	10	34.17	1.54	245	84
Untreated	—	41.94	2.07	734	91

oped by C.I.B.A. Aktiengesellschaft, Basel [2]. Here again the fabric is impregnated with a solution of a melamin-formaldehyde precondensate, but there are two differences with the „acid-colloid”-process mentioned before.

In the first instance, the precondensate applied in the Arigal-C finish, can be considered to consist of a more or less monomeric compound, whereas in the „acid-colloid” process a partly polymerized product is used. Secondly the „curing” step — and this is very essential for the Arigal finish — is applied when the fabric is in a moist condition. Although the rotproofing effect of both types of finish is excellent, as is shown in Table 1, there is some difference as to the influence of the treatments on the mechanical properties of the fabric.

From Table 2 it is clear that the mechanical properties of the fabric are impaired by the „acid colloid” treatment. The type and degree of this impairment is comparable to that of a usual crosslinking treatment of cotton. However, recent results of research, carried out at the Southern Regional Research Laboratory in New Orleans (La), show [3] that partial hydrolysis of „acid colloid” — treated fabric restores the mechanical properties to a large degree without an unallowable loss of rot-resistance of the fabric thus treated. Figure 1 shows the influence of the Arigal-C finish on the fabric properties. It is remarkable that when „wet fixation” is applied, the loss of mechanical proper-

ties is negligible whilst a severe loss of properties occurs when the resin is formed in the absence of moisture. On the other hand, a rotproof effect is only obtained with „wet fixation”.

The mode of action of the Arigal finish is not yet completely understood. Probably, also in this case, resin is formed in the more accessible regions of the fibre, although it is likewise possible that crosslinking of the cellulose molecules occurs; either chemical links between resin and the cellulose molecules or just a physical entanglement. The Arigal process in fact thus takes a position in between passive protection on a sub-microscopical and that on a molecular level, which will now be discussed.

In protection on a *molecular level*, the cellulose is chemically modified in such a way that it can no longer be degraded by cellulase. A well-known example is the partial acetylation of cotton. When a cotton fabric is treated in a suitable acetylation mixture, the reaction can be regulated in such a way that a relatively large percentage of the hydroxyl groups of the cellulose molecule is acetylated whilst the fabric properties are more or less kept intact (Fig. 2). A fabric becomes rotproof when about one third of the hydroxyl groups of the cellulose groups of the cellulose has reacted. From other measurements it is known that something of the order of one third of the cellulose molecules in a

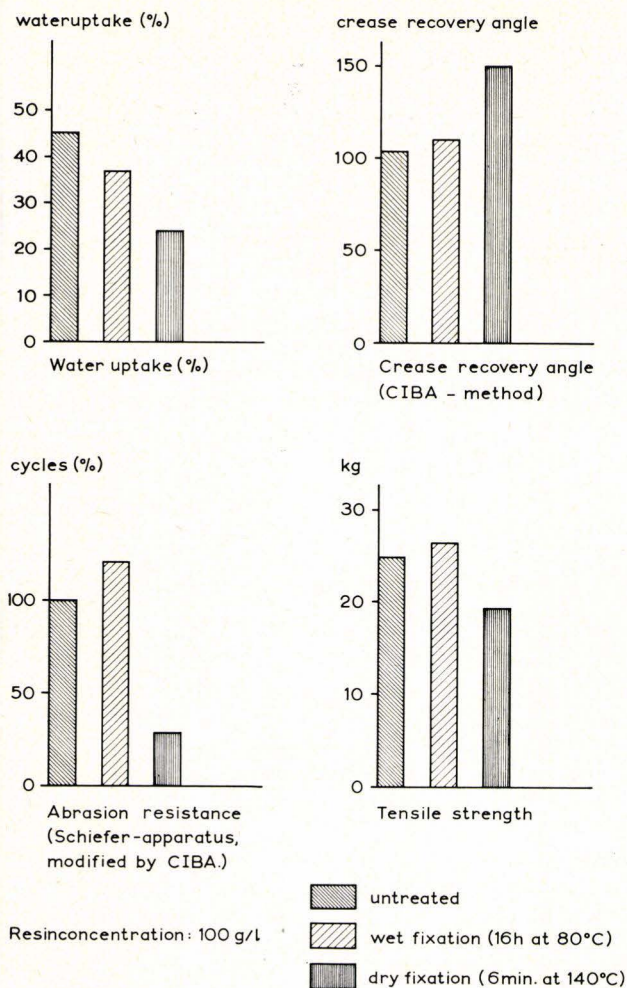


Fig. 1. Influence of „Arigal-C” treatment on some fabric properties.
(Curing step carried out „wet” and „dry”).

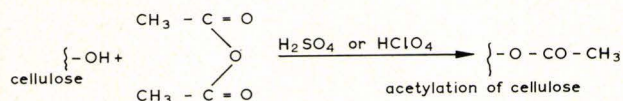


Fig. 2. Acetylation of cellulose.

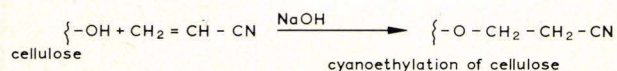


Fig. 3. Cyanoethylation of cellulose.

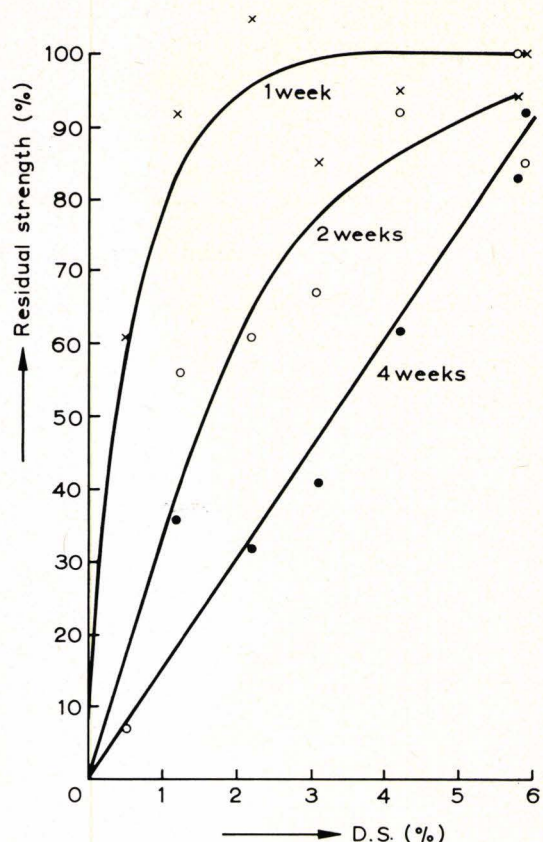


Fig. 4. Residual strength in the soil burial test of chloroacetamide samples at different degrees of substitution.

cotton fibre is more accessible for various chemical reactions.

It is therefore reasonably safe to suggest that the acetylation reaction has been restricted to these accessible regions in the fibre. As microbiological attack — at least in its first stage — is likewise restricted to these same regions it seems justified that the invading systems are confronted with more or less completely transformed cellulose.

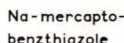
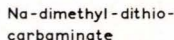
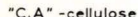
Another example of passive protection by chemical modification of cellulose is cyanoethylation (fig. 3). The high degree of rotproofness, attained by acetylation and cyanoethylation is shown in Table 1. Both processes have been worked out for application in practice, but largescale application is held up by the high cost of treatment and the rather specialized installations.

“C.A.-process” for passive protection of cotton

In our laboratory another method was worked out which is more or less comparable to the earlier mentioned methods: the C.A.-process. This method resulted from a series of attempts to bind fungicides or bactericides chemically to the cellulose molecules, in search of a wash-fast rotproof or bactericidal finish. The idea was to introduce into the cellulose molecule a reactive chlorine atom, followed by exchange of the chlorine atom by a suitable biocidal compound. Chlorine atoms were first introduced by means of the reaction:



The fabric was then aftertreated with a number of fungicides, for example:



From figure 4 it can be seen that at a degree of substitution ¹⁾ of about 6 a reasonable protection in the soil-burial test is attained. This is a very low D.S. when we compare it with the required D.S. in the acetylation process, where about 100 side-groups per 100 glucose units are necessary to obtain the same results. It would lead too far beyond the scope of this colloquium to discuss the process and its theoretical background in detail; only a few remarks will be made. In the first place the process has the same drawback which we also encountered in the Acid-Colloid process: the treatment gives a loss in tensile strength of the fabric of 20-30%. Such a loss of strength nearly always occurs when cotton is chemically modified. In fact, as far as I know, the only process which does not show such a loss of strength is the Arigal finish. Also practice has shown that the rotproofing effect is of the marginal type: sometimes excellent results are obtained, but when the soil is for some reason or the other more aggressive, the results are less convincing. A further remark is that chloroacetamide itself is non-toxic to micro-organisms. We modified the process in such a way, however, that also active protection was attained. For this purpose we used the following reaction:

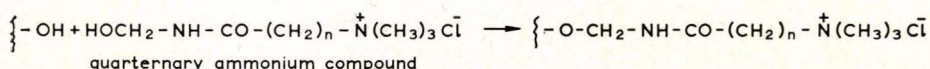
In the methods discussed so far, the fibres were made resistant to attack by cellulase, but there was no direct action on invading fungus and bacteria. In the soil test the fabric is not destroyed, but it can be overgrown with micro-organisms. On the

In fact, nearly all rotproofing treatments in practice are based on the application of fungicides. Most of them are applied in a very simple way: just impregnation and drying. However, an ideal treatment has still to be found: many compounds are coloured, and the effect is usually not sufficiently durable to leaching or washing. For a discussion of various types of fungicides, see the paper of Dr. Pauli in this journal. An example of a combination of active and passive protection is the Arigal PMP process, where in the melamin-formaldehyde resin a fungicide is incorporated.

The difference between passive and active protection of cotton textiles will now be illustrated with the results of two experiments, carried out in the Central Laboratory TNO ²⁾).

1) The degree of substitution (D.S.) is defined as the number of side groups per 100 glucose units. (One glucose unit contains three hydroxyl groups).

2) The results discussed here should be considered as being of a preliminary nature. A full account will be published elsewhere.



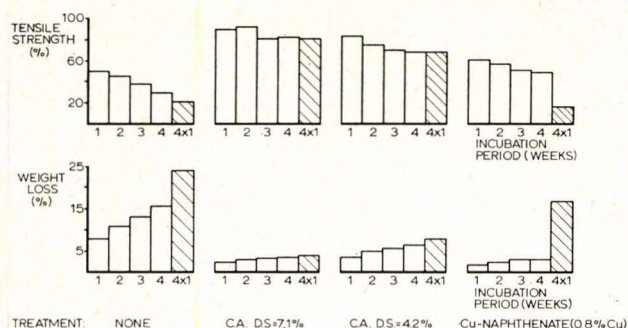


FIG. 5. TENSILE STRENGTH AND WEIGHT LOSS OF COTTON STRIPS AFTER TREATMENT WITH CELLULOSE OF *TRICHODERMA KONINGII* FOR DIFFERENT PERIODS.

Table 5

Storage test on cotton samples after 0, 6, 12 and 18 months of outdoor exposure.

The first experiment, carried out by W. Hazeu, concerns the application of cell-free cellulase extracts for the evaluation of rotproofed cotton. The organism *Trichoderma koningii* was cultured with cellulose powder as a carbon source. By filtration a cell-free extract was obtained, containing the enzyme cellulase.

Strips of cotton fabric were kept in the extract for a number of weeks. The samples included cotton, treated with chloro acetamide (a passive treatment), a sample treated with copper (active treatment) and, an untreated sample. After periods of 1, 2, 3 and 4 weeks a number of strips was harvested; and in a fifth series the sample was kept for 4 weeks in the extract but the extract was renewed each week. After harvesting, the tensile strength of the strips was determined; and by comparing the strength of the incubated strips with the strength of the strips before incubation, an impression can be gained of the effect of incubation.

In a parallel series, the loss of weight during the incubation was measured. In fig. 5, which shows the results of this experiment, the difference between passive and active protection is very clear. Especially in the case where the incubation extract was renewed each week, copper-naphthenate does not show any protection at all, whilst the passive protection remains. It is evident that an active treatment aims at killing the organisms, but it cannot prevent the enzymes from doing their work. On the other hand, the enzymes are not able to attack the passively treated sample.

Outdoor exposition of army tents, manufactured from "actively" and "passively" treated cotton

A second experiment concerns a large scale outdoor exposition of army tents. For this experiment, carried out in close co-operation with the Dutch Military authorities, and a number of manufacturers of textile fungicides, tents were manufactured from a standard cotton fabric treated with a number of rotproofing chemicals. Passive as well as active rotproofing methods were chosen. The passive treatments included the Arigal finish and the

chloro-acetamide process, both of which have already been discussed. The following active treatments were chosen upon consultation with the Quartermaster General:

1) *cunilate* a product of Scientific Oil Compounding Cy. The active component is copper-8-hydroxy-chinolate. This fungicide is widely used, especially in the U.S.A.:

2) *preventol* G.D. from Bayer A.G. Leverkusen. This product is also known as D.D.M. dichlorodihydroxydiphenylmethane.

From experience in our laboratory it was known that this is a very potent and a rather durable preparation, especially when it is fixed with copper.

3) *mystox* L.S.L.-special, from Catomance Ltd., U.K. This product contains pentachlorophenol-laurate as an active compound. It is widely used, also in the Netherlands. According to our laboratory experience, it is not very stable to light and neither is it very durable to leaching. It seemed therefore interesting to include mystox in our programme.

All compounds were applied together with a water-repellent finish. As blanks we used the same fabric, provided only with a water-repellent finish, together with a completely untreated fabric.

For each of the five methods of rot-proofing selected, eight tents were available.

Realizing that the climatological conditions have much influence on the behaviour of the cloth, three exposition locations were chosen, viz.:

Woerden (open space)

Beverwijk (open space behind the dunes)

Amersfoort (under trees)

The Beverwijk site was different from that at Woerden; Beverwijk is nearer to the sea. It was expected that the ultra-violet part of sunlight would here play a more important role in the attack of the cloth than in places further inland. In the course of experiments it was found, however, that the Beverwijk site was unfavourably situated with regard to the chemical industry (blast furnaces) in its environment. Accordingly, it had to be taken into account that vapours from this industry might cause chemical attack of the cloth. The exposition under trees was included in the programme to compare the behaviour of the cloth with that upon exposition in the open field; under trees there is usually a rather high relative humidity of the air. The conditions under trees will be more favourable for development of micro-organisms, also because any tents that have become wet will dry less quickly due to the protection of the trees than will tents exposed in the open field.

With intervals of six months, a quarter part of each tent was replaced by a new part. The harvested part was subjected to soil burial tests at the laboratory, half of the sample serving as blank material. By comparing the tensile strengths of these blank

Table 3

Exposition of army tents, manufactured from differently treated cotton fabric residual strength of fabric strips, obtained from exposed tents.

Treatment	location	Woerden				Beverwijk				Amersfoort			
	time of exposure months	6	12	18	24	6	12	18	24	6	12	18	24
Arigal		83	75	73	65	82	77	75	69	103	103	106	99
CA-process		75	58	61	51	69	66	72	65	92	91	97	90
Cu-8-oxychinoline		64	51	50	44	63	52	58	53	93	84	83	77
DDM		67	49	48	40	61	56	55	49	98	87	88	80
LPCP		60	53	52	43	63	49	48	48	91	92	85	80
waterrepellent		66	55	53	47	61	53	55	46	86	86	86	81
untreated	(36)	47	47	44	57	32	18	0	88	79	77	70	

Table 4

Exposition of army tents, manufactured from differently treated cotton fabrics: residual strength of fabric strips, obtained from exposed tents (exposure time same as in table 3), buried for two weeks afterwards.

Treatment	location	Woerden				Beverwijk				Amersfoort			
	time of exposure months	6	12	18	24	6	12	18	24	6	12	18	24
Arigal		109	100	71	45	98	98	75	67	101	100	95	98
CA-process		96	94	83	69	91	102	97	99	100	98	97	98
Cu-8-oxychinoline		43	34	23	17	46	30	16	11	21	15	10	8
DDM		70	36	25	20	72	28	17	16	24	24	13	11
LPCP		10	11	10	11	6	11	3	9	80	13	2	4
waterrepellent		12	21	20	14	21	17	13	11	4	15	10	10
untreated		0	0	13	11	0	0	0	0	0	0	4	7

strips with the tensile strength of the original material, an impression was gained as to the weatherability of the means of impregnation used.

By comparing the tensile strengths of the buried strips with those of the blank strips, an impression was gained as to the measure of rot-proofness still present at the moment of harvesting.

The soil-burial tests were carried out by method Vitno Bio A1. For the purpose, the strips were buried in a mixture of equal parts of leafmould, sand and horse dung.

The whole was incubated for 14 days at $29^{\circ} \pm 1^{\circ}\text{C}$ and $87.5 \pm 2.5\%$ relative humidity. After the experiment, the tensile strengths of the buried strips were determined, together with those of the non-buried strips.

After exposure, some strips of fabric were subjected to a storage test. For the purpose they were put in close touch with non-treated cotton fabric containing ca 70% of the air dry weight in soil suspension. This suspension had been applied by means of a laboratory jigger. The tensile strengths of the tent sections subjected to storage tests were expressed in per cent. of the corresponding tent sections that had been exposed only.

The calculation of these percentages aims at an impression of the value of the impregnations applied, if the cloth, after exposition in dirty condition, is stored under conditions favouring development of micro-organisms. The results of the experiment are shown in Table 3-5.

Two main conclusions can be drawn:

1) When we compare the results of Amersfoort (under trees) with those at Beverwijk and Woerden (in the open) it can be seen that the attack in Amersfoort was much slighter than that in the two open places. Apparently the biological attack expected in Amersfoort was of less importance than the actinic degradation in Woerden and Beverwijk.

2) For all cases a water-repellent finish offers an equally good protection as an active treatment with fungicides.

Another conclusion to be drawn is that the blank sample in Beverwijk is more rapidly degraded than the untreated tent in Woerden. This is probably due to the action of industrial gases. It is, however, evident that a water-repellent treatment can prevent this degradation.

Fig. 5. Tensile strength and weight loss of cotton strips after treatment with cellulase of *Trichoderma koningii* for different periods.

Rotproofing treatment	Residual strength (%) after storage test of 4 weeks duration carried out on fabric after months of outdoor exposure.			
	0 months	6 months	12 months	18 months
Arigal	104	102	100	100
CA	101	98	95	94
Cu-8-oxychinoline	102	95	44	55
DDM	102	95	73	77
LPCP	111	55	(0)	(34)
Water repellent	56	28	30	24
Untreated	25	11	(31)	0

Table 5 shows the result of the storage test, where samples of differently treated cotton fabric were stored in a moist condition as was described above.

It can be seen that all treated materials show up excellently in the storage test, provided that they have not been exposed. After exposure, the difference between active and passive protection again becomes evident.

Final Conclusion

The experiments discussed in this paper justify the final conclusion that in a moderate climate, like that of the Netherlands, biological degradation is generally not so very important. Other factors, especially actinic degradation, are usually of more importance.

As a large part of our national production of cotton materials is being exported, the desirability of rot-proofing for export purposes is beyond any doubt.

Literature

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