LXVI. THE ACTION OF SEA WATER ON COTTON AND OTHER TEXTILE FIBRES.

By CHARLES DORÉE.

From the Chemical Department, Borough Polytechnic Institute, London, S.E.

(Received October 11th, 1920.)

THE rapid disintegration of textile fabrics when exposed to sea water is well known. Under the condition of complete immersion most textile fibres become completely rotten in three to five weeks. The scientific interest attaching to the decomposition of such resistant materials as cotton and linen by the action of sea water is considerable. It is also of great importance to the marine biologist and others to discover the cause of this destructive action, leading either to a method of protecting fabrics, or to the production of a resistant material. The present paper contains a description of some experiments made with these objects in view.

The general effect of sea water is well illustrated in the following Table I which contains the results of trials carried out in the large tank of the Brighton Aquarium for which I am indebted to Dr J. Lyster Jameson.

Table I. *General Effect of Sea Water on various Textiles.*

+ indicates no obvious sign of weakening. ± visible deterioration. - completely rotten.

	Description	Examined after		
		Three weeks	Five weeks	Ten weeks
1.	Cotton fabric	-	...	...
2.	„ „ treated spermaceti	-	...	...
3.	„ „ treated spermaceti and ironed	+	-	...
4.	„ „ tanned with cutch	-	...	...
5.	Linen fabric	+	-	...
6.	„ „ treated spermaceti and ironed	+	+	-
7.	„ „ tanned with cutch	+	-	...
8.	Worsted fabric	+	+	±
9.	„ „ tanned valex*	+	+	+
10.	Silk fabric	+	-	...
11.	„ „ treated spermaceti	+	+	-
12.	Viscose silk	-	...	...

* This gave way completely in the next four weeks.

The fabrics were mounted in square frames and weighted so as to float vertically with the top edge just awash. After a week nearly all the materials showed a flocculent deposit, apparently bacterial and diatomaceous in

character, which readily shook off, leaving the fabric with a greasy feel which suggested the presence of organisms closely attached to the fibres. Green and rusty brown spots then appeared and gradually the fabrics disintegrated.

As will be seen cotton will not endure an immersion of three weeks, and linen and silk stand less than five. The spermaceti treatment (used by fishermen for preserving their lines) makes very little difference, an interesting result which may be due to the fact that spermaceti, as an ester, is possibly decomposed by micro-organisms. A better mixture would no doubt be paraffin wax combined with a softening agent. The tanning process mentioned consisted of a treatment with 5 % dichromate solution at 60°–65° for one minute. The material was then worked in a 3 % tanning solution (valex or cutch) for one minute and the process repeated several times. The spermaceti treatment was carried out by immersion for 15 minutes in a bath composed of spermaceti two parts, liquid paraffin B.P. 1 part at about 65°.

The tanning of vegetable fibres, however, has little influence, but the author has recently obtained a better result by tanning cotton for one hour at 70° in a 0.05 % tannin solution and then fixing by immersion in solutions of metallic salts the metals of which are toxic to bacteria. With copper a "life" of nine weeks was secured, though antimony and zinc made little difference.

The Chemical Changes produced in Cellulose by the action of Sea Water.

To ascertain the chemical changes produced in cellulose fibres a purified madder bleach calico was used. Test pieces were exposed¹, P in the light, Q in the dark. P soon became covered with pink growths which then disappeared to a considerable extent leaving rusty stains. In three weeks P was falling to pieces while Q, though whole, was quite rotten. P gave the following results:

	%
(a) Loss of weight in boiling 1 % NaOH (5 mins)	17.44
(b) Loss of weight in boiling 1 % NaOH (60 mins)	17.70
(c) Loss of weight in cold 17.5 % NaOH (20 mins)	19.15
(d) Hygroscopic moisture	6.09
(e) Copper reduced	1.42

The original madder bleach cotton gave under (a) 0, under (b) 0.6 % loss, (d) and (e) are normal figures. Of the part soluble under (c) only 20 % was reprecipitated by acid.

It is obvious that a very profound change is produced in the cellulose, as 17 % has become soluble in dilute sodium hydroxide solution. The fact that practically nothing more dissolves on further boiling points to the action being superficial and progressive.

¹ These and all subsequent trials were made for me at the Marine Biological Station, Plymouth.

The respective influences of Oxygen, Light and Micro-organisms.

The variables involved in the action of sea water on cellulose are oxygen, light, and bacteria or mould growth. To study their influence a series of laboratory experiments was set up in which all or none of these conditions were present and each was excluded in turn. Pieces of the standard madder bleach calico were placed in large flasks or jars full of sea water obtained from Lowestoft. Suitable devices were used to ensure freedom from oxygen or bacteria, and the immersion was continued in each case for nearly two years except in that of Exp. E, which was removed at the end of one year.

In Table II, which follows, will be found details of these experiments and in Table III the analytical constants of the pieces exposed.

Table II. *Influence of Oxygen, Light and Bacteria: Experimental details.*

Exp.	Weight in grams	Time in months	Exposed to			Notes on Experiments
			Oxygen	Light	Bacteria	
A	22.68	21	○	○	○	5 litres of sea water in flask, boiled with the cotton air-free and allowed to fill completely from a second flask permanently attached. Added HgCl_2 about 1 part in 2000. Conditions well maintained throughout. Cotton yellowish at end.
B	54.66	20	+	+	○	8 litres in covered glass jar. Water kept covered with toluene and oxygenated frequently by blowing purified air.
C	47.00	21	○	+	+	5 litres; oxygen removed by blowing hydrogen for 3 hours. Large bolt-head flask completely filled, with pipette through cork for expansion, etc. Freedom from air well maintained—fabric brownish at end.
D	27.94	22	○	+	○	A duplicate of A; fabric brownish at end.
E	40.46	12	+	○	+	8 litres; large stone jar exposed to the air and oxygenated frequently.
F	35.00	22	+	+	+	5 litres; oxygenated frequently and kept in good light. Growths appeared and disappeared from time to time.

All weights given in this paper are "dry" weights calculated at water-oven temperature.

The moisture was always determined on a separate piece of fabric weighed simultaneously.

Table III. *Analytical Constants of the Cotton after immersion.*

Expt.	Exposed to			Relative strength of warp threads	Change in weight %	Ash %	Loss of weight % on boiling with 1% NaOH		Copper reduced %
	Oxygen	Light	Bacteria				5 mins.	60 mins.	
Original cotton	...	...	...	100*	...	0.13	0.00	0.50	2.4
A	○	○	○	126	+0.3†	0.21	0.07	0.42	2.4
B	+	+	○	124	-0.4	0.17	0.16	0.21	1.7
C	○	+	+	107	-0.6	0.16	0.10	0.65	2.3
D	○	+	○	105	+0.8†	0.12	0.52	0.64	1.9
E	+	○	+	85	-2.4	0.21	1.80	1.90	2.8
F	+	+	+	79	-2.0	0.11	0.83	0.97	2.4

* The actual breaking load was 123 grams.

† Due no doubt to the property of cellulose of fixing mercury from mercuric chloride (Vignon). This was present in Exps. A and D.

These results show clearly that if bacterial growth is prevented sea water as such has no action on cotton. Exps. A and B show practically the same values as the normal cotton, light and oxygen by themselves appearing to be without effect (Exp. B). The curious increase in strength shown by the first four samples is possibly due to shrinkage. On the other hand Exps. E and F, in which micro-organisms and oxygen were present, show marked deterioration comparable in kind, though not in degree, with Exps. P and Q made in the sea. They show a distinct loss in strength and in weight and in addition the remaining cellulose exhibits a solubility of nearly 2 % in sodium hydroxide which is not increased by more prolonged boiling. Light seems to have a slightly accelerating influence on the rate of destruction.

This series of experiments points strongly to the conclusion that bacterial or mould growth is the cause of the destruction of cotton fibres by sea water and that the presence of oxygen is essential.

This conclusion was supported by microscopic evidence. The investigation of a somewhat similar problem, viz. the deterioration of cotton on wet-storage, by Fleming and Thaysen [1920] led to the result that cotton stored damp is not affected unless micro-organisms are present, and not then if the moisture content of the cotton is reduced below 9 %. Finding it impossible to study microscopically the changes in the structure of the fibre brought about by the micro-organisms, these authors applied the modification of the viscose reaction suggested by Balls.

After treatment with the alkali-bisulphide mixture the fibres immersed in water swell to five times their normal size bursting the cuticle if it remains uninjured. In the paper mentioned, photographs are given showing the result of this test.

(a) With the normal fibre, presenting the appearance of a series of bulbs connected by rings of cuticle.

(b) With the fibres damaged by a streptothrix which has destroyed the cuticle and also perforated the fibre in many places causing it to break up into short pieces (fly).

(c) With the fibres damaged by a cellulose-decomposing schizomycete which eats away the cuticle over large areas and causes a progressive destruction from the surface to the interior.

The cotton fabrics E and F which were most affected by exposure to sea water when submitted to similar tests showed of course a large number of normal fibres. A considerable proportion, however, gave evidence of cuticular damage, and in each case the appearance was exactly that assigned by Fleming and Thaysen to the cellulose-decomposing schizomycete. This was abundantly proved by an examination of specimens P and Q (17 % soluble in NaOH). In this case practically every fibre showed evidence of the schizomycete—the streptothrix action was not observed.

The Nature of the Change produced in Cotton by the action of Sea Water.

Some conclusions as to this can be drawn from the figures obtained in these experiments. Numerous trials as with P and Q show that complete disintegration of the cotton takes place. On drying, the piece readily breaks up into a dusty powder. Yet except in the important matter of solubility in alkalies, the material shows very little difference from the normal cellulose. The pieces dyed with methylene blue and benzopurpurin to the same extent as the original fabric. The formation of a reducing substance such as oxycellulose which is almost invariably the result of chemical attack is excluded by the fact that the copper numbers in Table III are identical with the normal value¹. The action of the micro-organisms would seem to be mechanical and in this connection it is of interest to recall the observations of Cross and Bevan [1918] on the destructive breakdown of cotton fibre under the mechanical process of beetling. A "cellulose dust" is formed which in its proximate composition, copper reducing power, dyeing and mercerising qualities etc., resembles normal cellulose. On treatment with 17.5 % sodium hydroxide in the cold, however, only 44 % remains undissolved and of the 56 % in solution only 48 % is reprecipitated by acids. These curious changes are being critically studied, and the results obtained in the present paper certainly show a similarity which is worth recording. Some marked change takes place in the cellulose complex which results in an entirely new direction of cleavage under the influence of alkali and yet permits of the retention of other characteristic properties.

Hess and Wittelsbach [1920] regard cellulose as a complex built up of "cellulose" (hydrocellulose) molecules united by the residual valencies of the hydroxyl groups. They suggest that the physical characteristic of cotton as a hollow thread is reproduced in the arrangement of the cellulose molecules in the complex, and that this complex can be broken down by mechanical means producing changes similar to those resulting from moderate chemical treatment.

It is exceedingly probable that the change whatever it may be is conditioned by the reactivity of the three hydroxyl groups of the cellulose unit formula and it appears not unlikely that if some or all of these were acetylated or otherwise "protected" the cellulose complex would be unable to rearrange itself in the direction of alkali solubility, and loss of structural character and the deterioration due to beetling or to micro-organisms might not take place. A suggestion on these lines was put forward by C. F. Cross eight years ago and two cotton fabrics were acetylated by his method approximately to the stage of a mono- and a di-acetate respectively, the structural form of the cotton being retained. These pieces were immersed in sea water at the same time as those detailed in Table I. No growths were visible at any time, and when the fabrics were removed after 16 weeks they appeared completely

¹ These numbers though very much higher than usually found for a purified cellulose were done by a standard method and are comparable

unaffected. The process can be carried out by such a method as that of Eng. Pat. 142,615 of Oct. 1919. One part of fused zinc chloride is dissolved in a mixture of acetic anhydride 5 or 6, glacial acetic acid 4 or 5 parts. The cotton is treated several times with double its weight of this mixture at temperatures below 50°. It is very difficult, however, to acetylate an open fabric such as muslin without largely sealing up the openings and the process is not of much use for marine biological purposes.

Cellulose Acetate Silk, a resistant Textile Material.

Attention was therefore directed to the "Acetate Silk" now being manufactured on a large scale by British Cellulose and Chemical Manufacturing Ltd. from the soluble cellulose tri-acetate. Yarns of every grade of fineness are now available and by the courtesy of the Sales Department a supply was sent for experiment.

An acetate silk twist yarn with a breaking load of 3.2 kilos was immersed in sea water under the same conditions as those of Exps. P and Q. At the end of five weeks no growths had appeared, the fibres seemed quite unchanged and the breaking load was still 3.0 kilos. Even after four months no appreciable change had taken place.

It will be seen therefore that a material is at length available which has a satisfactory resistance to sea water. At present fabrics composed wholly of acetate silk are not being manufactured, mixed fabrics only being produced. The yarn is available in any quantity, and it is recommended that this be knitted into suitable meshed fabrics for marine biological use.

SUMMARY.

1. Fabrics of cotton and silk are destroyed by immersion in sea water for three weeks, wool lasting somewhat longer.
2. This destructive action has been shown in the case of cellulose to be due to micro-organisms and not to oxygen, light or the salts present.
3. In its nature it resembles the "mechanical" break-down of cotton sometimes observed under the "beetling" process.
4. If cotton is acetylated to the mono-acetate stage so that its structural qualities are preserved, the resulting material is very resistant to sea water.
5. Cellulose acetate silk now manufactured on a large scale has proved able to withstand the action of sea water for months.

I desire to express my thanks to Dr E. J. Allen, F.R.S. of the Marine Biological Station, Plymouth, for his valuable cooperation throughout this investigation, for the expenses of which I am indebted to a grant from the Dixon Fund of London University.

REFERENCES.

- Cross and Bevan (1918). *J. Soc. Dyers Col.* **34**, 215.
Fleming and Thaysen (1920). *Biochem. J.* **14**, 25.
Hess and Wittelsbach (1920). *Zeitsch. Elektrochem.* **26**, 232.