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From the State Veterinary Serum Laboratory, Ringsted, Denmark.

COTTON AND POLYESTER UDDER TOWELS

A STUDY OF THEIR REACTION WITH HALOGEN-CONTAINING DISINFECTANTS*)

By

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There is an important variation in the bactericidal effect of sodium hypochlorite against Staphylococcus pyogenes depending on whether the bacteria are embedded in a cotton cloth or suspended in a solution.

Eaton (1964) discovered that 50 mg chlorine**) per l of chlorinated water killed Staphylococcus pyogenes in less than 15 sec. On the other hand, *Foot* (1962) obtained an unsatisfactory disinfection of udder cloths in 3 min. with chlorinated water containing 600 mg chlorine per l. This observation can be partly explained by the fact that it is difficult to free the staphylococci from the fibres of the cloth (in contrast to Escherichia coli (*Walter* 1955)).

The great variation in the bactericidal effect of chlorinated water in the circumstances described cannot be explained just by the attachment of the staphylococci to the cotton threads. Other factors also appear to play a rôle.

Possible reasons for the diminishing content of chlorine in chlorinated water with udder cloths are:

I. Evaporation of chlorine.

II. Diffusion of chlorine through the walls of the container, or reaction with the materials of the container.

*) The investigations were supported by Statens teknisk-videnskabelige Fond.

**) Unless otherwise stated "chlorine" and "iodine" mean "total available chlorine" and "total available iodine", respectively.

III. Splitting off of oxygen from the hypochlorite ions. The oxygen can then disappear as explained under I and II.

IV. A chemical change in the chlorinated water itself.

V. A reaction between the cotton and the chlorine.

In the present study these possibilities have been investigated. Furthermore, cotton udder cloths and polyester sponges have been compared as regards their reactions with solutions of hypochlorite and iodophor.

MATERIAL AND METHODS

The cotton cloths used had a loose-spun vigogne thread in one direction and a tightly woven knitwear thread at right angles above it (quality 4707).

Polyester foam is produced by mixing, under pressure, liquid polyester with isocyanate and water. When the pressure is released as the mixture leaves the mixing machine, a liberation of carbon dioxide occurs, which results in the formation of the foam structure (the "blowing"). The blowing is furthered by addition of catalysts ("blowing agents").

When silicones are added to the polyester before blowing, the carbon dioxide bubbles (the cells) will be evenly distributed and of uniform size. It is possible to control the size of the cells by using different silicones, temperatures and blowing agents.

The polyester foam K2485*) has the following characteristics:

Density: 36.6 kg/m^3
Elongation: 215 %
Tensile strength: 16.4 lb/inch^2
Indentation hardness: 25 % deflection: 29.4 kg/50 inch^2
50 % deflection: 40.8 kg/50 inch^2
65 % deflection: 52.3 kg/50 inch^2
Second 25 % deflection: 23.1 kg/50 inch^2
Tear resistance: 2.1 lb/inch
Cell structure: about 14 cells/cm.

The cotton cloths designated "used" were prepared by placing new cloths for 18 hrs. in a solution of sodium hypochlorite at 12—20°C (1000 mg chlorine per l) or in a solution of iodophor (200 mg of iodine per l) at the same temperature. The cloths were wrung out firmly before use.

*) Kindly supplied by Dansk Polyether Industri.

Solutions of sodium hypochlorite were prepared from a stock solution*) containing 15.5 % chlorine and an alkali excess of 21 g sodium hydroxide per l. A freshly prepared solution with 530 mg chlorine per l had a pH of 9.1.

Solutions of iodophor were prepared with Iodophor 302-2**). A freshly prepared solution of this iodophor containing 120 mg iodine per l had a pH of 2.6.

The concentration of chlorine in solutions of sodium hypochlorite was determined by titration after the method of *Slagteriernes Forskningsinstitut* (The Danish Meat Research Institute) 1966, with the following modifications:

To avoid acid precipitation of sulphur and growth of bacteria, sodium carbonate was added to the solution of sodium thiosulphate.

The starch indicator solution was preserved with mercury iodide (*Vogel* 1966).

The content of iodine in iodophor solutions was determined with sodium thiosulphate solution using the so-called "dead-stop end-point" titration (*Linnet* 1964). Usually a titration lasted for 5 min.

The significance of the factors mentioned under points I to IV have been investigated in the following way: 24 new, respectively "used", cotton cloths were put into a solution of sodium hypochlorite at 40°C. The cloths were removed one by one at intervals of 2—3 min. The investigations were performed at room temperature (22°C). The temperature of the sodium hypochlorite was therefore falling at the same rate as during udder wash in practice.

As a control an experiment was performed also with a solution of sodium hypochlorite without cotton cloths. A light stirring every 2—3 min. made up for the agitation caused by the removal of the cloths.

Trials were performed also at other temperatures, using the following technique:

Six identical cotton cloths were placed for 2 hrs. in chlorinated water with 1000 mg chlorine per l. After being wrung out to uniform weight the cloths were evenly distributed in 3 buckets with 4 l of sodium hypochlorite solution in each (concentration

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*) Kindly supplied by Dansk Soyakagefabrik.

**) Kindly supplied by Sunlight Fabrikkerne.

412 mg per l). One bucket was held at 90°C, one at 45°C, and one at 20°C. The concentration of chlorine was determined 2 or 3 times in the course of 20 min.

The extent to which a single cotton cloth will neutralize and adsorb chlorine was investigated using the following technique:

Three two-l glass beakers with glass covers were used.

In beaker I, 1.5 l of tap water, 20 ml of the stock solution of sodium hypochlorite and one new cotton cloth were placed.

In beaker II, 1.5 l of tap water and 20 ml of the stock solution of sodium hypochlorite were placed.

In beaker III, 1.5 l of tap water and a new cotton cloth were placed.

In beakers I and II the chlorine content was 3100 mg at the start. The temperature of the water in the three containers was the same in each trial, but varied from one trial to the other (as shown in Table 1). The beakers were kept in a thermostat at constant temperature for 5 hrs. Stirring every hour.

After 5 hrs. the cotton cloths were taken up and wrung out so that the liquid ran back into the respective beakers.

The amount of chlorine neutralized or adsorbed by the wrung-out cloths (C) may be calculated by the formula

$$C = (A - B)(1.5 + 0.02 - 0.044)$$

A stands for mg of chlorine per l in beaker II after 5 hrs.; B for mg of chlorine per l in beaker I. The figures 1.5, 0.02 and 0.044 indicate, on a litre basis, the amounts of, respectively, water, stock solution of sodium hypochlorite, and liquid in the wrung-out cloth.

The content of chlorine in a wrung-out cloth was determined as follows: The cloth was placed in a beaker to which was added 200 ml 0.01 N sodium thiosulphate, 20 ml 4 N sulphuric acid and 7 g potassium iodide, making a total of 223 ml liquid. After 4 min. the cloth was removed and wrung out, and 100 ml of the liquid was placed in another beaker suited for titration. Before titration 10 ml 0.1 N potassium bichromate was added. For the titration the same thiosulphate solution was used as mentioned above (T ml). The titration was repeated once. The amount of chlorine in the cloth ($X_{c.c.}$ mg) was calculated from the formula $X_{c.c.} = 0.3546\ (2.67\ T - 67)$. This assessment can be tabulated by comparing the corresponding amounts of oxidizing and reducing materials in the titration beaker. (The cloths were wrung out in such a way that 44 ± 1 g liquid was left in each).

The method employed for the determination of the amount of chlorine in a wrung-out cloth implies that the result ($X_{c.c.}$) will depend to a very great extent on factors such as light intensity, oxygen in the air, possible evaporation of chlorine, time between adding of potassium bichromate solution and titration, and possibly other factors as well. To assess the importance of these sources of error, it was necessary to carry out a blank experiment: beaker III (without sodium hypochlorite). By means of beaker III an X_{blank}-value was determined by the same method as the value $X_{c.c.}$. The chlorine content in the wrung-out cloth would then be $X_{c.c} - X_{blank}$.

Polyester sponges were examined in a corresponding way. A polyester sponge weighed 15 g and contained 15 ± 1 g chlorinated water after pressing. Consequently the amount of chlorine neutralized or adsorbed by the sponges was $C = (A - B)(1.5 + 0.02 - 0.015)$. The content of halogen in a pressed sponge (X_{pol}) also had to be corrected by subtraction of an X_{blank}-value, determined as for cotton cloths.

Similar experiments with iodophor solution were carried out on the reaction of cotton cloths and polyester sponges. The procedure was as described above, but with the following modifications: The iodine content at the start was 402 mg in beaker I and II, potassium iodide was not added, and stirring was omitted. The amount of iodine in a wrung-out cloth was determined as mentioned for chlorine, but with the following modifications: Instead of 200 ml 0.01 N sodium thiosulphate, 220 ml was used. The amount of iodine ($X_{c.c.}$ mg) was

$$X_{c.c.} = 1.2692\,((240 + J)\,T\,0.01 - 20 - J)$$

where J = g iodophor solution in the wrung-out cloth. For this special investigation the iodophor Wescodyne*) was used.

RESULTS AND DISCUSSION

The decrease in the concentration of chlorine in solutions of sodium hypochlorite with and without cotton cloths is shown in Fig. 1. The decrease is obviously due to the presence of the cotton cloths, even if a very small decrease is seen also in the solution without cloths.

*) Kindly supplied by Ciba.

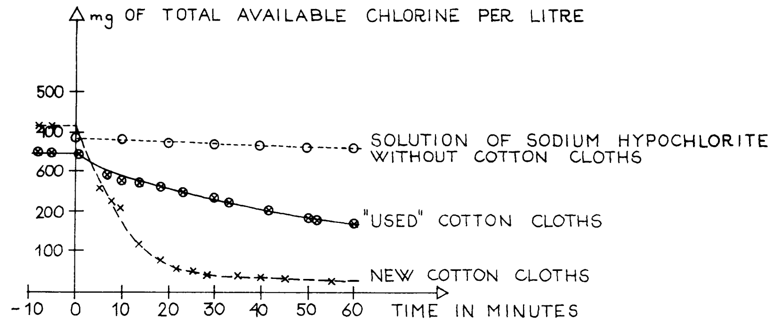


Figure 1. Concentration of chlorine in solutions of sodium hypochlorite with or without cotton cloths. (Method: "A separate cloth per cow". Start temperature: 40°C; room temperature: 22°C).

The results of a corresponding trial with solutions of Iodophor 302-2 are given in Fig. 2.

From the graphs in Figs. 1 and 2 it appears that new cotton cloths reduce the halogen content to a greater extent than "used" cloths. The shape of the graph for new cotton cloths in Fig. 2 may be explained by the fact that the 24 cloths were lying close together in the bucket; for this implies that at the start the iodophor-solution will mainly have attacked the outer parts of the cloths. As the upper cloths were removed, and the iodophor-solution got better access to the cloths lying underneath, the neutralization of iodine will have accelerated.

The temperature of a solution of sodium hypochlorite with cotton cloths has a great influence on the content of chlorine.

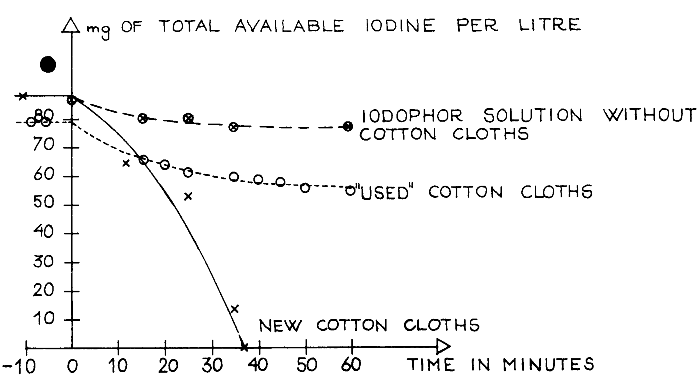


Figure 2. Concentration of iodine in solutions of iodophor with or without cotton cloths. (Method: "A separate cloth per cow"). Start temperature: 40°C; room temperature: 22°C).

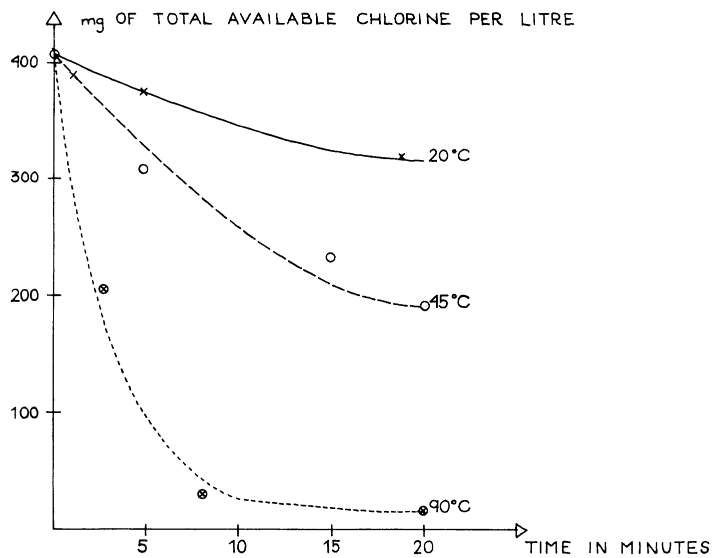


Figure 3. Concentration of chlorine in three portions of chlorinated water with two cotton cloths in each.

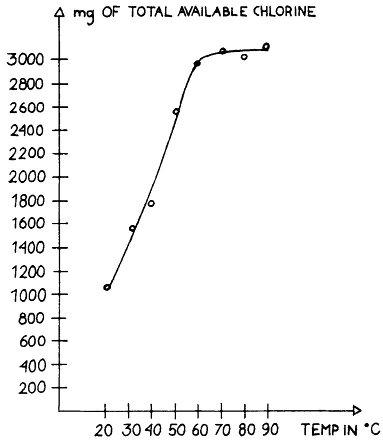
Fig. 3 shows that the neutralization accelerates with increasing temperature.

The extent to which cotton cloths neutralize and absorb halogens at different temperatures appears from Figs. 4—7. Concerning Figs. 5 and 7, X_{blank} turned out to be —4 mg chlorine and —1 mg iodine, respectively.

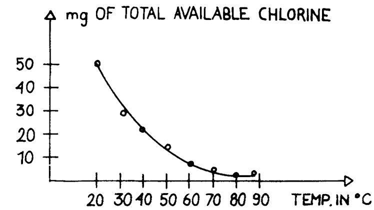
The halogens found in the wrung-out cloths can be assumed to be bound partly to the fibres of the cloths and partly to the liquid between the fibres. The possible maximum of halogen in this liquid is indicated in lines C (in Table 1) and L (in Table 2).

From Fig. 4 it appears that the neutralization of chlorine increases up to 50—60 °C, but beyond 60 °C the graph is deflected, obviously due to the fact that all the chlorine (3100 mg) has been neutralized or adsorbed. Presumably the neutralization would have continued to increase if more chlorine had been present.

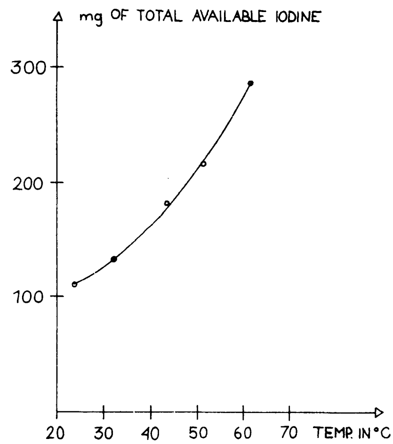
There is a considerable similarity between Figs. 4 and 6, and also between Figs. 5 and 7. However, differences are seen as well. For instance, at 31 °C 14.2 % of the neutralized or adsorbed iodine, but only 2.2 % of the chlorine, were recovered from the wrung-out cloth (calculated from the graphs). The difference is



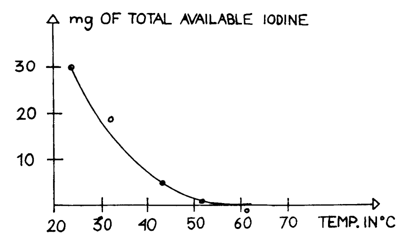
F i g u r e 4. The amount of chlorine neutralized or adsorbed by the cotton cloths.



F i g u r e 5. The amount of chlorine in the wrung-out cloths.



F i g u r e 6. The amount of iodine neutralized or adsorbed by the cotton cloths.



F i g u r e 7. The amount of iodine in the wrung-out cloths.

probably due to the fact that iodine is a less powerful oxidizing agent than chlorine.

When chlorine disappears from chlorinated water, sodium hydroxide may remain in the solution, which will therefore still exert some inhibitory effect on growth of bacteria. However, pH also declines (Fig. 8) due to the chemical reactions mentioned below.

Table 1. Neutralization and adsorption of chlorine by cotton cloths in solutions of sodium hypochlorite.

Temperature in °C	20	31	40	50	60	70	80	88
A = mg chlorine per l in beaker II after 5 hrs.	2046	2053	1982	2016	2039	2042	2011	2038
B = mg chlorine per l in beaker I after 5 hrs.	1340	1014	794	307	60	14	7	4
C = possible maximum of chlorine (mg) retained in the 44 g liquid of the wrung-out cloths = 0.044 × B	59	45	35	14	3	1	0	0

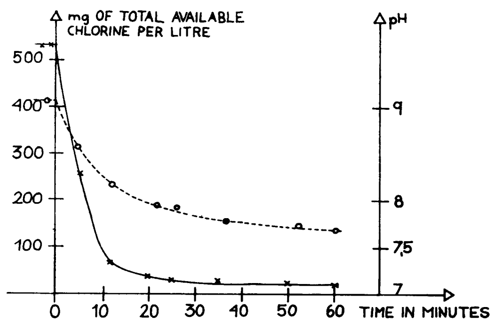


Figure 8. The relation between fall in pH and amount of chlorine. (Method: "A separate cloth per cow"). ——— mg chlorine per l. - - - - - pH.

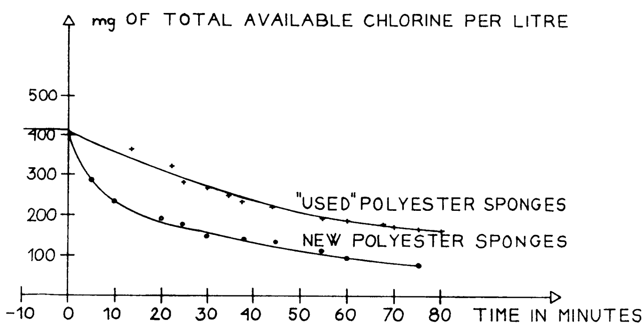


Figure 9. The concentration of chlorine in a solution of sodium hypochlorite with 24 polyester sponges. (Method: "A separate sponge per cow". Start temperature: 40°C; room temperature: 22°C).

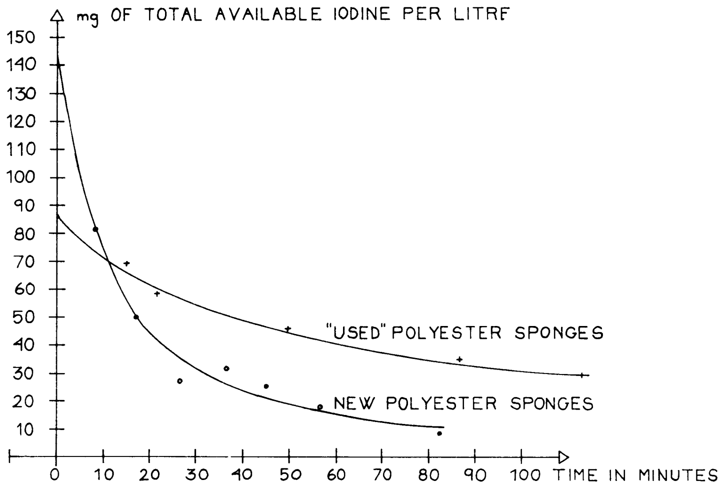


Figure 10. The concentration of iodine in a solution of iodophor with polyester sponges. (Method: "A separate sponge per cow". Start temperature: 40°C; room temperature: 22°C).

Table 2. Neutralization and adsorption of iodine by cotton cloths in solutions of iodophor.

Temperature in °C	23	32	43	51	61
F = mg iodine per kg solution in beaker II after 5 hrs.	263	251	245	236	227
G = mg iodine in total in beaker II after 5 hrs. = $1\frac{1}{2} \times F$	395	377	367	354	340
H = mg iodine per kg solution in beaker I after 5 hrs.	195	169	125	94	37
J = g iodophor solution in the wrung-out cloths	47	46	42	41	40
K = mg iodine recovered in beaker I = $H(1500 - J)\ 0.001$	284	246	182	137	55
L = possible maximum of iodine (mg) retained in the liquid of the wrung-out cloths = $H \times J \times 0.001$	9.1	7.7	5.2	3.8	1.5

Results concerning polyester sponges appear from Figs. 9 and 10. It is obvious that considerably more halogen is neutralized by new polyester sponges than by used sponges.

Table 3. Neutralization and adsorption of chlorine by polyester sponges in solutions of sodium hypochlorite.

Temperature in °C	22	31	40	50	60	70	80
A = mg chlorine per l in beaker II after 5 hrs.	1881	1941	2057	2064	2027	2042	2011
B = mg chlorine per l in beaker I after 5 hrs.	1854	1789	1592	1053	135	21	11
C = possible maximum of chlorine (mg) in the liquid retained in the pressed sponges = 0.015 × B	28	27	24	16	2	0.3	0.2

Table 4. Neutralization and adsorption of iodine by polyester sponges in solutions of iodophor.

Temperature in °C	23	30	37	50	61
F = mg iodine per l in beaker II after 5 hrs.	267	260	256	245	214
G = mg iodine in total in beaker II = F × 1½	400	390	385	367	322
H = mg iodine per l in beaker I after 5 hrs.	107	100	96	74	44
J = g liquid in the pressed sponges	7	6	8	6	6
K = mg iodine left in glass I = H × (1500—J) × 0.001	160	149	144	110	66
L = possible maximum of iodine (mg) in the liquid retained in the pressed sponges = J × H × 0.001	0.8	0.6	0.8	0.4	0.3

The rate of neutralization and adsorption of halogens by sponges at different temperatures appears from Figs. 11—14. Concerning Figs. 12 and 14, X_{blank} turned out to be —1 mg chlorine and —1.9 mg iodine, respectively.

It appears from Fig. 11 that the rate of neutralization and adsorption of chlorine by polyester sponges is low at temperatures under 45°C.

Some of the chlorine which disappeared from the solution was reversibly bound to the sponges. It will be seen from Fig. 12 that at temperatures up to 60°C the amount thus bound increased

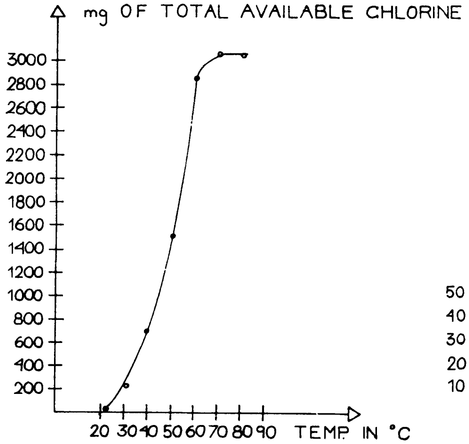


Figure 11. The amount of chlorine neutralized or adsorbed by the polyester sponges.

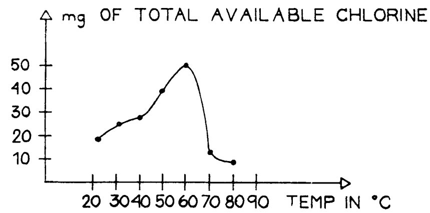


Figure 12. The amount of chlorine in the present polyester sponges.

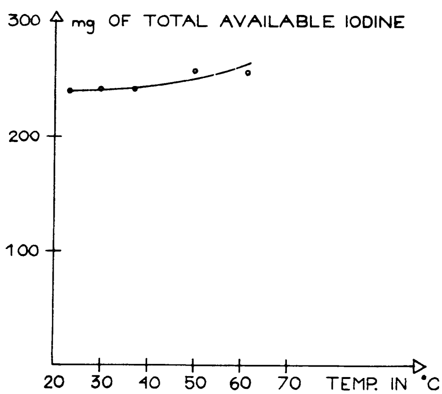


Figure 13. The amount of iodine neutralized or adsorbed by the polyester sponges.

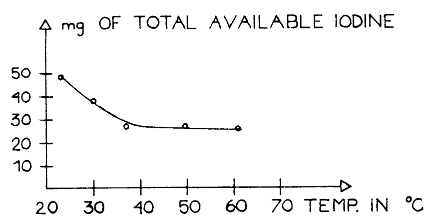


Figure 14. The amount of iodine in the pressed polyester sponges.

with temperature, while it decreased when the temperature rose from 60°C to 80°C.

From Fig. 13 it appears that, within relevant ranges, the neutralization and adsorption of iodine were almost independent of temperature.

Some of the iodine which disappeared from the solution was reversibly bound to the sponges in amounts decreasing with temperature within the range from 23°C to about 40°C. At temperatures from 40°C to 61°C the amount of iodine reversibly bound was constant (Fig. 14).

In the light of the results reported above, and considering the chemistry of cotton, it is possible to draw a parallel between the reaction of cotton cloths with hypochlorite solution and the bleaching process applied in the textile industry.

The main constituents in cotton is cellulose, which can be regarded as a polymer of glucose (100—12500 molecules). The formula is outlined in Fig. 15 (*Jørgensen* 1966).

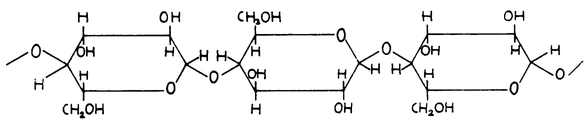


Figure 15. Formula of cellulose.

The longer the chains, the stronger the cotton (a high degree of polymerization). The degree of polymerization may be calculated by chemical methods (*Rath* 1963).

Under alkaline conditions the reaction between cellulose and chlorinated water is probably an oxidation and not a chlorination (*Rath*). The oxydation is most likely due to development of (nascent) oxygen

$$HClO \rightarrow HCl + (O) \text{ and } ClO^- \rightarrow Cl^- + (O)$$

The released oxygen may attack the cellulose in several ways, by which under alkaline conditions some depolymerization usually takes place and acid groups are formed. The formation of acid groups explains the decrease in pH demonstrated in Fig. 8.

Other constituents of cotton than cellulose, however, are more easily oxidized. This most likely explains the differences seen between new and "used" cotton cloths, as shown in Figs. 1 and 2.

As to the optimum temperature of udder-wash water, no agreement exists between authors.

Wilson (1955) and *Zaks* (1962) advance the idea that by using water as hot as practicable the milk erection is stimulated.

According to *Sykes* (1958), the bactericidal effect of chlorinated water is likely to increase with rising temperature.

Whittleston (1949) did not find a stimulation of the milk "let-down" by using hot udder-wash water.

Johns (1954) did not find any increase in the bactericidal effect of chlorinated water when the temperature was raised from 5°C to 20°C and 45°C.

The results of the present study seem to suggest that a temperature not exceeding 45—50°C in an udder-wash with hypochlorite and cotton cloths is optimal. At temperatures over 45—50°C the content of chlorine will fall owing to an accelerated reaction with the fibres of the cotton cloths (and contaminating material). A high temperature of the solution will therefore presumably hamper its disinfecting effect on milkers' hands, partly because the concentration of chlorine will often have fallen to too low a level, partly because the milkers will avoid putting their hands into the very hot water.

It is reasonable to attribute the unsatisfactory disinfection of cotton udder cloths by solutions of sodium hypochlorite to the reaction between cotton (and contaminating material) and chlorine.

Unpublished field studies by the author have shown that polyester sponges are fully acceptable as replacement for cotton udder cloths and in certain respects even preferable. With polyester sponges it is easier than with cotton cloths to maintain a sufficient halogen level; most likely this is due mainly to a lower content of dirt in the sponges. As to chlorine, the differences appearing by comparison between Figs. 4 and 11 also seem to be of importance. Proper polyester sponges, however, neutralize and adsorb more iodine than cotton udder cloths under relevant conditions (cf. Figs. 6 and 13).

CONCLUSION

It has been shown that the temperature of hypochlorite solutions should not exceed 45—50°C, especially when the udder-wash method "a separate cloth or sponge per cow" is used.

Furthermore, the results indicate that cotton is not an ideal material for udder cloth, because it neutralizes chlorine as well as iodine to an undesirable degree. This fact is especially unfortunate as far as chlorine is concerned, because the neutralization is rather pronounced and milkers have no chance of controlling the strength of the chlorinated water.

A recommendable alternative to cotton udder cloths is polyester sponges, which neutralize chlorine to a more limited degree, bind halogens reversibly, and are easier to clean.

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SUMMARY

Inactivation of chlorine and iodine by cotton cloths was found to be most pronounced at temperatures over 45°—50°C, and new cloths had a greater inactivating power than used ones.

Polyester sponges were found to inactivate less chlorine but more iodine than cotton cloths. To some extent, both halogens were bound reversibly to the polyester.

SAMMENDRAG

Bomuldsklude og polyestersvampe til yveraftørring.
En sammenligning af reaktionen med halogenholdige desinfektions-midler.

Det vises, at bomuldsklude er i stand til at neutralisere halogener. Dette forhold er især udtalt for nye bomuldsklude og ved temperaturer over 45—50 °C. Det tilrådes derfor til yveraftørring med bomuldsklude at bruge klorvand med en temperatur under 45—50 °C. De uheldige virkninger er især udtalte ved metoden „én klud pr. ko".

Som alternativ til bomuldsklude foreslås polyestersvampe anvendt. Disse svampe er ganske vist også i stand til at neutralisere klor, men i mindre omfang end bomuldsklude. Endvidere binder de halogener reversibelt og er lettere at rengøre.

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