Study on Deodorant Fabric Softeners

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Abstract

It has been demonstrated that the long chain alkyltrimethyl ammonium salts of phenolic germicides, such as pentachlorophenol and 2,2′-methylene-bis-(3,5,6-trichlorophenol) showed remarkable substantivity to cellulosic fiber, much more than that of the phenolic germicides alone, without lowering of the bacteriostatic activity and deodorant effectiveness.

Introduction

The simple phenolic derivatives, for example, p-cresol and o-phenylphenol, are widely used as skin cross-disinfectants and as sanitizers for hard surface such as ceramic tile and linoleum in hospitals (1–3). However they have little significant residual action and substantivity to fabrics or skin (2). Pentachlorophenol (PCP) also has ability to kill microorganisms, but its toxicity and skin irritation are more pronounced than common soap bacteriostats, for example, 2,2′-methylene-bis (3,5,6-trichlorophenol), G-11 Sindar Co., popular name: hexachlorophene. PCP is therefore not used in toiletry goods as a bacteriostat. Hexachlorophene is stated in many reports to have a wide antibiotic spectrum against disease germs or other harmful microorganisms and high substantivity to the skin (4–7).

According to Stuart, alkyltrimethyl ammonium salt has also considerable disinfectant ability against enterobacterium and vegetative gram-positive bacteria such as *Staphylococcus aureus* and *Bacillus subtilis* (3). Domagk has reported that alkyltrimethyl ammonium salt containing an alkyl chain longer than 16 carbon atoms decreased antibacterial effect against *S. aureus* as compared with shorter alkyl chains such as 12 and 14 (8). Toilet bars and household laundry products which contain antibacterial agents have recently been used to keep surroundings bacteriologically clean. A medicated soap is made to inhibit infections and also as a liquid cleanser for hard surfaces (2).

Weatherburn and Bayley (9) studied the absorption of cationic and anionic surfactant cellulose materials from an aqueous solution. It was shown that deposition of cetyltrimethyl ammonium bromide compared with sodium laurylsulfate in molar concentration, was about 7 and 15 times greater at pH of 3.5 and 9.0 respectively. According to Sexsmith and Namba, by changing the anions of quaternary ammonium salts, the magnitude of absorption is in the reverse order of the strength of the ionic bond, $I^- > Br^- > Cl^- > F^-$ (10,11). At concentrations greater than critical micelle concentration, cationic surfactants were noted as causing so-called ion-pair absorption. Cetyltrimethyl ammonium bromide absorbs both the quaternary ammonium cation and anion on cellulosics over concentrations of 1.0×10^{-3} mol/l (10–14 and Katsumi and Kawanaka, private communication).

On the basis of the above-mentioned references, we believed that long chain alkyltrimethyl ammonium salts of a phenolic germicide should be available as a bacteriostat and a softening agent. As the typical phenolic germicide, PCP and hexachlorophene were used. Stearyltrimethyl ammonium pentachlorophenate and hexachlorophene-stearyltrimethyl ammonium salt were solubilized by a cationic surfactant. Socks were treated with the solution of PCP- and hexachlorophene-quaternary ammonium salt and were tested for deodorant and bacteriostatic effectiveness. The absorption of PCP and quaternary ammonium pentachlorophenate by cotton gauze was measured from an aqueous alcohol solution to determine the relation between substantivity and bacteriostatic effectiveness.

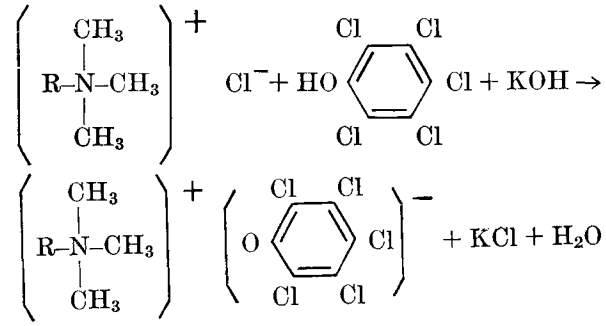
TABLE I
Elemental Analysis of PCP-86P and G-11-86P

Product	Calcd. Cl (%)	Calcd. N (%)	Found Cl (%)	Found N (%)	m.p. °C	Appearance
PCP-86P	31.0	2.4	30.8	2.4	88–90	white crystal
G-11-86P	29.9	2.0	30.1	1.9	134.5–135.5	white crystal

Experimental Procedures

Materials

The quaternary ammonium salts of phenolic germicides were synthesized in the presence of potassium hydroxide. One mole of stearyltrimethyl ammonium



$R = C_{18}$ and C_{16}

chloride (86P. M.W. 342.4 Kao Soap Co., trade name: Quatamin 86P) and one mole of Pentachlorophenol (PCP, Mitsui Chemicals Co. M.W. 266.4) were dissolved into 1,280 ml of methanol. Then one mole of KOH (M.W. 56.11) dissolved in 600 ml methanol was added with drops for 30 min. Methanol and water were distilled off at temperatures below 50 C in a current of nitrogen gas. The crude product was recrystallized twice with 2,000 ml of acetone. The product was named PCP-86P. Hexachlorophene-quaternary ammonium salt (G-11-86P) was also made by the same method. Their elemental analyses are shown in Table I.

Determination of Deodorant Effectiveness

In order to provide repeatable sampling, 100% cotton socks were preferred to determine deodorant effectiveness. PCP-86P or G-11-86P solution solubilized with stearyldipolyethoxymethyl ammonium chloride (P = 10 SEAC, Kao Soap Co.) were used to treat the socks.

Composition A was the following: PCP-86P (or

TABLE II
Concentrations of PCP and PCP-86P Solution

PCP (ppm)	70	50	30
PCP-86P (ppm)	124.1	88.7	53.2
Molar conc. (mole/l)	2.627×10^{-4}	1.877×10^{-4}	1.126×10^{-4}

TABLE III
Deodorant Effectiveness of Composition A Containing PCP-86P Against Contrast

Grade	Cycle 1 L–R	1 R–L	2 L–R	2 R–L	3 L–R	3 R–L	4 L–R	4 R–L	5 L–R	5 R–L	Percentage
+2	3	4	7	5	15	13	9	8	5	4	18.8
+1	16	15	20	19	14	17	18	19	16	17	44.1
0	18	16	6	9	10	8	6	7	11	11	26.3
−1	3	5	4	4	1	2	7	6	3	4	10.1
−2	0	0	1	1	0	0	0	0	1	0	0.7
Small total	19	18	28	23	43	41	29	29	21	21	100.0
Total	37		51		84		58		42		
Variance ratio	13.4**		15.9**		59.5**		20.1**		11.6**		

G-11-86P), 2%; SEAC, 2%; water, 96%. In contrast, composition B was: SEAC, 2%; water, 98%. Halves of 20 pairs of socks were immersed in 0.1% A solution for 3 min at 25 C and squeezed to 200% weight. The other halves of the socks were treated with 0.1% B solution. Each pair of socks was worn by each of 20 young assistants for 4 hr. The intensity of unpleasant odors on the socks was graded by two trained persons who divided them into the following five classes (15): remarkable contrast recognized, +2; contrast recognized to some degree, +1; no contrast recognized nor any odor in either of the socks, 0; reverse contrast recognized to some degree, −1; remarkable reverse contrast recognized, −2.

Deodorant effect was determined by making an analysis of variance using Scheffe's paired comparison method.

Determination of Bacteriostatic Activity

Cotton swatches, 2 × 2 cm, were sewed on the toes of the socks turned inside out and they were treated using the compositions A and B under the same conditions in order to determine the effectiveness of the deodorant (4,6,7). After the socks had been worn for 8 hr, the swatches were cut off and washed with 10 ml of normal saline solution for 2 min. One milliliter of the diluted solution was added to 10 ml of brain heart infusion broth. All tests were incubated at 36 C for 48 hr and visible strains were counted.

Determination of Substantivity

Twenty grams of cotton gauze swatches were dipped in a liter of solution shown in Table II at 30 ± 0.5 C. Aqueous alcohol (1:1 w/w) was used as a solvent. The pH was adjusted to 4.8 with acetic acid for PCP-86P and sodium carbonate for PCP. The ultraviolet absorption method was used for determination of PCP and PCP-86P, which exhibit sharp absorbance at 321 and 323 mμ respectively. The Shimazu AQV-50 type digital spectrophotometer was employed (16).

The calibration curves for optical density and the concentration of PCP and PCP-86P gave a linear function through the origin and the following equation was obtained:

$$Y = 9.546 \times 10^{-3}X \qquad [1]$$

Y is optical density and X is the concentration of PCP or PCP-86P. The substantivity to cotton was measured from concentration of the remaining solution by the following equation (9,10 and Katsumi and Kawanaka, private communication).

$$\frac{(C_{n-1} - C_n)\, V_n}{10W} + A_{n-1} = A_n \qquad [2]$$

where A_n and A_{n-1} = substantivity at n and n-1 times; C_n and C_{n-1} = concentration of the solution at n and n-1 times; V_n = aliquot portion withdrawn at n times and W = the weight of fabric.

Results and Discussion

The deodorant effectiveness values of the composition containing PCP-86P or G-11-86P are shown in Table III and IV respectively.

Double asterisks signify highly significant values. L–R means the smelling order from left sock to right sock and R–L the reverse. Because there was the possibility that the number of microorganisms or odor of the feet varied, the socks in pairs were worn at random for greater statistical reliability. Differences in the order of smelling were also examined as L–R and R–L, but no significance was recognized. According to the right side column of Table III, PCP-86P had a remarkable deodorant effect for 18.8% of the persons and had deodorant effect to some degree for 44.1% of the persons. No odor was detected for 67% of the persons ranked zero and no difference of odor was detected in the remainder. Reverse effect was observed for 10.8% of the persons checked. On the other hand, it is clear from Table IV that G-11-86P had remarkable deodorant effect for 23.5% of the persons and deodorant effect to some degree for 35.5% of the persons. No odor was detected for 70% of persons ranked zero, and reverse effect was observed for 6.5%. The variance ratios of the main effect are shown in Tables III and IV. From these data, it was recognized that PCP-86P and G-11-86P possessed significant deodorant effectiveness on the socks with less than 1% error.

The bacteriostatic activity results are shown in Table V. The concentrations of PCP-86P contained

TABLE IV
Deodorant Effectiveness of Composition A Containing G-11-86P Against Contrast

Grade	Cycle 1 L–R	1 R–L	2 L–R	2 R–L	3 L–R	3 R–L	4 L–R	4 R–L	5 L–R	5 R–L	Percentage
+2	16	10	10	8	8	12	8	14	10	8	26.0
+1	14	14	12	16	12	14	18	14	14	18	36.5
0	8	14	18	16	12	12	14	12	16	14	34.0
−1	2	2	0	0	8	2	0	0	0	0	3.5
−2	0	0	0	0	0	0	0	0	0	0	0
Small total	44	32	32	32	20	36	34	42	34	34	100.0
Total	76		64		56		76		68		
Variance ratio	45.4**		40.9**		20.7**		59.9**		48.8**		

TABLE V
Bacteriostatic Activity Test of Composition A Containing PCP-86P

Concentration of PCP-86P in composition A, %	Numbers of microorganisms		Per cent reduction of microorganisms	
	Treated with A	Treated with B	Per cent reduction	Average, %
2.5	5.0×10^2	7.44×10^4	99.3	99.5
	1.02×10^3	4.32×10^5	99.8	
	4.7×10^1	8.3×10^3	99.4	
2.0	8.0×10^2	1.96×10^4	95.9	96.8
	8.7×10^2	6.09×10^4	98.6	
	5.4×10^1	1.36×10^3	96.0	
1.75	5.86×10^3	1.45×10^5	95.9	94.2
	3.28×10^3	4.69×10^4	93.0	
	3.93×10^2	6.36×10^3	93.8	
1.50	9.6×10^2	9.8×10^3	90.2	90.5
	2.16×10^4	2.12×10^5	89.8	
	1.37×10^2	1.62×10^3	91.4	
1.25	8.06×10^2	5.6×10^3	85.4	83.9
	3.4×10^3	2.66×10^5	87.2	
	1.16×10^2	5.51×10^3	79.0	

in composition A varied from 2.50% to 1.25%. It was evident that PCP-86P exhibited a powerful bacteriostatic effect against bacteria such as *staphylococci* at a very low concentration.

Most of the microorganisms by the agar plate method were proved to be *Staphylococci* and *colitis* types by bacteriological identification. Composition A containing only PCP instead of PCP-86P was also tested, and the minimum inhibitory concentration was approximately 30 times greater than PCP-86P.

Evidence of the higher substantivity of PCP-86P over PCP to cotton fabrics is shown in Figure 1. The significance in using the phenolic germicide-quaternary ammonium salt was the increase in substantivity to cellulosic fabrics. The rate of exhaustion of PCP-86P was characteristic of quaternary ammonium salts. (9–13 and Katsumi and Kawanaka, private communication.) Furthermore the substantivity of PCP-86P from 88.7 ppm solution increased remarkably in comparison with that from 53.2 ppm solution. It would not be unnatural to consider from Sexsmith's theory that 88.7 ppm solution of PCP-86P had already exceeded the critical micelle concentration, and ion-pair absorption had occurred. It was found moreover that simple solutions of PCP-86P or G-11-86P or their compositions with another cationic surfactant had the possibility of increasing the "soft hand" of the fabric. Because long chain alkylquaternary ammonium salts of phenolic germicides showed high substantivity on a cellulosic fabric, and because they have high bacteriostatic action and remarkable deodorant effectiveness, they should become accepted as components of deodorant softeners.

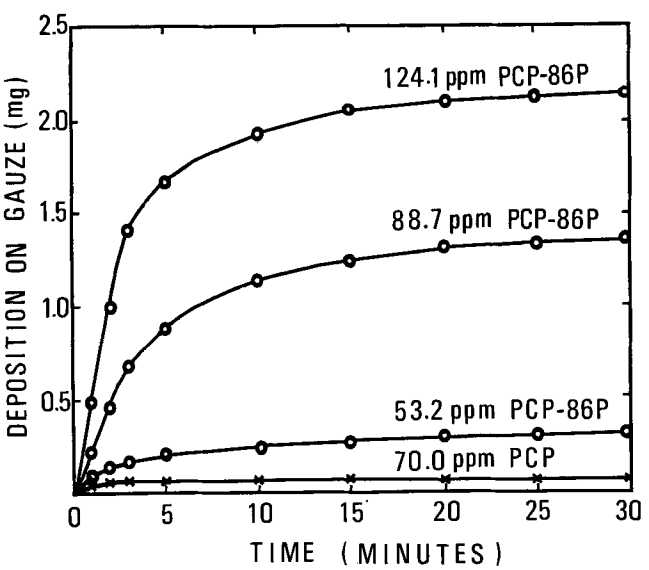


FIG. 1. The relationship of exhaustion rates and substantivities on cotton gauze between PCP-86P and PCP with concentration described in Table II. The data on PCP at concentrations of 50 and 30 ppm were abbreviated because of its low substantivity at low concentration.

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