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A Study of S-330 as an Impregnite for Permeable Protective Clothing

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A Study of S-330 as an Impregnite for Permeable Protective Clothing

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ABSTRACT

This report deals with a study of the compound S-330 as an impregnite for permeable protective clothing. Most of the work reported is based on an aqueous process of impregnation.

In comparison with other chloroamides used as impregnites, the compound S-330 was found to be quite stable on cloth, and to cause somewhat less deterioration of cotton fabric. The excellent retention of active chlorine and tensile strength for S-330 impregnated fabrics was maintained throughout a wide range of variations in impregnating systems.

Vesicant vapor penetration tests showed that S-330 was effective against Lewisite whereas other chloroamides gave very little protection. When H vapor penetration tests are made on cloth samples containing S-330, there is an initial period when H vapor penetrates the fabric. This initial leakage is particularly pronounced after storage or weathering. Many variations and procedures were investigated in an attempt to eliminate the initial unreactivity of S-330. No successful procedure was found.

The compound S-330 is not recommended as an impregnite for protective clothing since physiological tests have shown that it does not give adequate protection.

AUTHORIZATION

1. This work was authorized under Project 547/41, "Maintenance, Bureau of Ships," dated 16 December 1940. The problems which were proposed for study were given in Bureau of Ships letter S-S77-2 (Dz) Serial 811 of 17 December 1940.

STATEMENT OF PROBLEM

2. This study was undertaken to determine the suitability of the compound S-330 as an impregnite for protective clothing. The present Navy directive specifies the compound S-145. Preliminary studies showed that S-330 was superior to S-145 in certain important respects.

KNOWN FACTS BEARING ON THE PROBLEM

3. Preliminary work on impregnite S-330 was reported in a Memorandum to the Director entitled "The Evaluation of Impregnite S-330," dated 19 November 1942. The memorandum describes results obtained with S-330 applied to cloth by the tetrachloroethane solvent process. Impregnite S-330 appeared to be enough superior to impregnite S-145 to warrant exhaustive investigation.

4. Pilot plant production of S-330 at NRL has shown that the compound can be produced in quantity at a cost which compares favorably with that of S-145.

5. This Laboratory, the NDRC, and the CWS have been actively engaged in developing a protective ointment containing S-330. Numerous irritation tests of protective ointments have shown that S-330 is remarkably non-irritant among chloroamides. Furthermore, some indications have been obtained in wearing trials of protective clothing that S-330 is superior to other impregnites from the standpoint of irritation.

THEORETICAL CONSIDERATIONS

6. In order to establish the superiority of one impregnite over another, the four major factors listed below should be used for comparisons:

a. Retention of active chlorine by the impregnite under extreme conditions of storage, exposure, and wear.

b. Tendency to rot cotton fabric under extreme conditions of storage.

c. Reactivity toward vesicant vapors.

d. Irritancy under extreme conditions of wear.

The memorandum mentioned in paragraph 4, showed S-330 to be superior to S-145 in categories (a) and (b). It also showed that S-330 is unique among impregnites in that it offers protection against L.

7. The superiority of S-330 with regard to cloth tendering and its protection against L hasbeen attributed to the basicity of S-330 or S-330 base. S-330 base (unchlorinated S-330) contains two imino groups which are sufficiently basic to react with acids and form salts. It is believed that these imino groups in S-330 itself as well as in S-330 base can react with HCl and thus prevent cloth tendering. Furthermore, this ability to react with HCl would account for the protection afforded by S-330 against Lewisite vapor.

8. Another advantage possessed by S-330 over S-145 is that S-330 contains more than twice as much active chlorine per unit weight. This means that the same active chlorine loading can be obtained on a given area of cloth with about one half the weight of impregnite; conversely, the same loading weight of impregnite will furnish twice as much active chlorine.

PREVIOUS WORK DONE AT THIS LABORATORY

9. NRL Report No. P-2000 describes in detail the test methods employed in the evaluation of protective clothing. NRL Report No. P-2055 describes the aqueous system of applying impregnite to clothing. A Memorandum to the Director entitled "The Evaluation of Impregnite S-330," dated 19 November 1942, describes results obtained from protective clothing impregnated with S-330 by the solvent process. The memorandum also describes a laboratory method of preparation of S-330.

EXPERIMENTAL PART

A. Stability of S-330

10. Accelerated thermal and hydrolytic stability tests run on S-330 show it to be superior to S-145 in this respect. Tables I and II give the data. It will be noted that these and the succeeding tables characterize the S-330 with numbers such as P-2, P-3, and so on. During the early part of this work the available S-330 came from NRL's pilot plant which at that time was experimenting with the manufacture of S-330 under various conditions. The characterizations refer to different batch numbers.

Table I

Thermal Stability

Compound	% Cl+ Retained					
	100°C			70°C		
	2 days	1 mo.	6 mo.	2 mo.	6 mo.	8 mo.
S-330	-	97	13	-	97	-
S-330 + 10% ZnO	-	98	0.4	-	97	-
S-330 + 25% ZnO	-	98	0.5	-	98	-
S-330 + 15% Daxad 11	-	98	3.7	-	98	-
S-145	58	17	-	78	-	66
S-145 + 10% ZnO	0	-	-	84	-	68
S-145 + 25% ZnO	0	-	-	61	-	0

Table II

Hydrolytic Stability

(0.2 g. chloroamide, 5 hrs. in 100 ml. boiling water)

Compound	Particle Size	Added Agents	% Cl+ ret.
S-330 (P-6)	1-5 microns		75
	5-10		67
	10-20		77
	20-30		77
	30-40		71
	Mixture		73
	Micronized		80
S-145 (TCA)	1-3		54
	5-10		51
	10-16		71
	20-30		81
	44-53		88
	Mixture		85
	Micronized		40
S-330 (P-2)		+ 20% Daxad 11	92
		+ 3"x3" cloth	41
		+ 20% RH-403	81
		+ 20% Methocel	91
		+ 17% ZnO	57
		+ 75% CP in 36-C*	81

* Standard emulsion concentrate.

B. Formulation

11. The bulk of the work done on formulation was done with the S-330 as it came from NRL's pilot plant. This material had a particle size of 5-40 microns. NRL Reports No P-2055 and P-2124 demonstrated the superiority of small particle size impregnite S-145 in most respects. It was reasonable to assume that these advantages would extend to S-330 if the latter were of small particle size. Accordingly, a quantity of S-330 was micronized by the International Pulverizing Corporation and this material was used in further laboratory and plant impregnation of cloth. Micronized S-330 ranged from 1-5 microns and could be substituted for unmicronized in any formulation. The standard concentrated chlorinated paraffin emulsion described in the Navy directive for aqueous plant impregnation using S-145 was used throughout in these formulations. It will be referred to hereafter as 36-C. Typical formulations which were successfully used for impregnations are as follows:

(1) Laboratory formulation with Colloid Mill

20# of unmicronized S-330 (Batch P-7) and 1# of zinc oxide were stirred into 20# of water containing 3/4# Daxad 11. The slurry was recycled in an Eppenbach Colloid Mill until free from gritty matter. The microscope showed the powders to be well deflocculated with only a few small agglomerates. This slurry and 22.5# of 36-C were each diluted with 33# of water and then mixed. The mixture was then flocculated, but two passes through the mill at clearance zero gave satisfactory deflocculation. This impregnating bath contained 8% S-330. Army HBT suits, regulation underwear (long), and socks were impregnated from this bath, wrung out by hand, and tumbler dried. All had a good appearance and the active chlorine contents were as follows: Suits 1.1 mg. $Cl^+/cm.^2$; underwear 0.8; socks 0.8.

(2) Laboratory formulation with Gear Pump

A formulation without the use of the colloid mill and incorporating dye was as follows: 2400 g. of water containing 50 g. TLX-40, 10 g. TLX-42 30 g. Daxad 11, 500 g. S-330 (Batch P-7), and 50 g. ZnO was recycled through a gear pump until little or no grit could be felt. At this point not all the S-330 was deflocculated. Ten minutes additional recycling did not improve the slurry.

Added 1125 g. 36-C and recycled again for 10 minutes. Diluted to 8% S-330 and impregnated several swatches of Arnzen cloth. Although not all the S-330 had been deflocculated, the swatches, wrung out by hand, were evenly dyed with no heavy deposits, and the cloth contained 0.9 mg. $Cl^+/cm.^2$.

(3) Portable Plant Formulation

A plant run was made with the S-330 (micronized) as follows: To 90# of 36-C were added 36# of khaki dye solution (10% dye - 5 parts TLX-41 to one part TLX-42) and 24# of water containing 2# of Daxad 11. Using a "Lightnin'" mixer, 40# of micronized S-330 was stirred in. After stirring for 15 minutes, the S-330 was well deflocculated. 4# zinc oxide was added and stirred again. The zinc oxide did not deflocculate readily. The bath was diluted to 64 gallons (6.3% S-330) and used to impregnate five batches of eleven suits each of Navy Arnzen cloth suits, 50 pair of gloves, and 100 pair of socks. The standard procedure and equipment of the Navy portable impregnating plant was used. The suits were not as evenly impregnated as in the regulation S-145 process. This was attributed to the excessive foam that was encountered in the impregnation. The excessive foam may be due to the relatively large amounts of Daxad that are required to disperse the S-330. Foam was present in all formulations tried to date. The suits analyzed 0.63 mg. $Cl^+/cm.^2$ with a range of 0.42-0.81.

(4) Chlorination on fabric.

There is evidence that the distribution of chloroamide in the cloth has a pronounced effect on its behavior in respect to both weathering and reactivity toward H vapor. It was possible to obtain a thorough distribution of S-330 throughout the body of the cloth in the following manner. A strip of laundered Arnzen cloth was immersed in a water solution containing 7% ~~by weight~~ of S-330 base hydrochloride and was wrung out as dry as possible. Without letting the cloth dry completely, it was suspended in an atmosphere of chlorine gas for 20 minutes. The cloth was then thoroughly rinsed in

water and allowed to dry. The cloth was satisfactory in appearance and was soft and pliable. There was no appreciable dusting off except on violent beating. The active chlorine content was 1.0 mg./cm.^{2}. It was found that this figure could be controlled by varying the concentration of the original bath. The cloth could then be treated easily as required, as with an emulsion of chlorinated paraffin, a slurry of zinc oxide, or dye, or whatever might be necessary to achieve special properties.

Formulations using this technique will be designated as COF.

C. Evaluation of Impregnated Arnzen Cloth

12. The behavior of S-330 cloth on weathering was studied in the same manner as described in Report No. P-2055 for S-145. Two accelerated tests were used: Storage at 75°C and 75% relative humidity, and storage at 110°F and 75% R.H. Outdoor weathering was carried out by exposure at Miami, Florida, and at Washington, D. C. The effect of storage and outdoor exposure on active chlorine retention and retention of cloth strength was determined. The resistance of the impregnated cloth to vesicant vapors is taken up in a later section.

(1) Comparison of Chloroamides

13. Table III compares various chloroamides which have been under consideration from time to time. Arnzen cloth samples were impregnated from standard aqueous dispersion systems both with and without stabilizer. The cloths were then subjected to the storage and exposure tests. S-330 was generally superior to the other chloroamides especially when stabilized with 10% zinc oxide. For all the chloroamides, zinc oxide had a beneficial effect on tensile strength retention, and it improved the active chlorine retention of S-330 impregnated cloth.

14. Table IV compares cloths cut from suits that were impregnated for wearing trials. S-330 here was superior to the other compounds in respect to active chlorine retention.

(2) The Effect of Binder

15. The ratio of binder to chloroamide was studied in an effort to determine whether there was an optimum concentration as far as weathering and storage stabilities were concerned. The binder used in every case but one was the standard 42% chlorinated

Table III

Comparison of Chloroamides on Cloth

(Data given as percent of original values)

Compound	Stabilizer % ZnO*	Outdoor Exposure (Florida, May, 1943) Chlorine (Cl+) 1 wk	2 wk	3 wk	4 wk	Tensile (T.S.) 1 wk	2 wk	3 wk	4 wk	75°C-75 RH 96 hrs. Cl+	T.S.	110°F-75 R.H. Cl+ 30 da	T. S. 30 da	60 da	90 da	120 da
S-330(P-1)	-	56	40	26	14	95	88	74	54	56	90	77	100	95	82	78
S-330(P-1)	10	80	64	50	39	100	100	100	87	83	100	93	100	100	91	91
S-328	-	49	49	52	21	67	40	24	13	70	73	85	100	76	63	63
S-328	10	65	31	32	20	98	70	40	25	64	91	87	100	82	74	70
S-222	-	50	60	27	24	100	75	65	41	44	60	89	100	76	77	73
S-222	10	71	45	48	24	100	100	95	63	51	100	92	100	93	82	90
S-461	-	67	36	25	3	49	25	16	4	21	38	50	68	41	35	28
S-461	50	39	0	0	0	80	66	59	35	8	31	53	60	36	28	28
S-461	30% MnO_2	67	50	43	24	63	33	25	6	28	63	70	98	82	76	78
S-330(M)	-	62	52	45	26	94	82	71	55	51	88	78	100	91	81	82
S-330(M)	10	78	53	53	33	100	100	96	74	77	100	79	100	97	98	88
S-145	-	55	38	39	32	52	29	22	17	52	77	73	97	99	88	-
S-145	10	49	45	37	29	92	94	85	57	61	88	93	97	95	95	-
S-330 Micronized	-	85	67	65	-	100	100	91	-	87	92					87
S-330 Micronized	10	85	71	72	-	100	100	100	-	95	97					100

* Based on Chloroamide

Table IV

Comparison of Chloroamides on Cloth
(Data given as percent of original values)

Compound	Stabilizer % ZnO*	Outdoor Exposure (Washington, June, 1943) Chlorine (Cl^+) 1 wk	2 wk	3 wk	4 wk	Tensile (T.S.) 1 wk	2 wk	3 wk	4 wk	75°C-75% RH 96 hrs. Cl^+	T.S.	110°F-75% RH 30 da Cl^+	T.S.
S-145**	15	56	27	41	15	88	76	74	67	50	93	29	94
S-145	25	46	26	30	17	95	87	88	72	57	98	35	96
S-330	10	43	53	43	43	88	88	97	69	82	97	100	100
S-461	20+5% $MnAc_2$	87	65	33	17	89	59	28	21	87	80	56	67

**Solvent Impregnation
*Based on chloroamide

Table V

Effect of Binder Content on Stability of S-330 (P-5).
(Data given as percent of original values)

Binder % C. P.*	Stabilizer % ZnO*	Outdoor Exposure (Washington, June, 1943) Cl+ 1 wk	Cl+ 2 wk	Cl+ 3 wk	Cl+ 4 wk	T. S. 1 wk	T. S. 2 wk	T. S. 3 wk	T. S. 4 wk	75°C-75 R. H. 96 hrs. Cl+	75°C-75 R. H. 96 hrs. T.S.	110°F-75 R. H. 30 days Cl+	110°F-75 R. H. 30 days T.S.
None	0	65	59	56	39	100	99	69	67	89	100	50	88
25	0	86	51	49	33	100	100	69	66	73	100	45	98
50	0	81	52	46	32	100	95	65	66	61	100	38	91
75	0	77	60	44	40	100	92	67	56	69	100	44	97
None	10	87	68	69	53	100	100	100	90	94	100	80	96
25	10	92	67	57	43	100	100	100	94	85	100	100	100
50	10	86	65	55	56	100	100	96	89	100	100	81	98
75	10	82	59	54	49	100	100	96	96	93	100	100	100
**75 Min. Oil	10	69	56	52	40	100	--	--	96	110	100	41	99

* Based on Chloroamide
** Weathered August, 1943.

paraffin (CP). In one case a heavy refined mineral oil was used. The cloths were impregnated with aqueous dispersions prepared from unmicronized S-330 as previously described. The data are given in Table V. No marked differences are evident among samples containing different amounts of binder. A similar series carried out with micronized S-330 showed the same behavior. The data is shown in Table VI.

Table VI

The Effect of Binder Content on Micronized S-330
(Data given as per cent of original values)

Binder % CP	Stabilizer % ZnO	Outdoor, Florida December, 1943 Cl+ 1 wk	Cl+ 2 wk	Cl+ 3 wk	T.S. 3 wk	75°C-75% RH 96 hrs. Cl+	75°C-75% RH 96 hrs. T.S.	110°F-75% RH 60 da Cl+	110°F-75% RH 120 da Cl+	110°F-75% RH 120 da T.S.
0	0	86	72	68	100	89	93	79	67	94
25	0	82	67	69	100	91	93	79	67	86
50	0	87	67	70	96	88	85	76	63	89
75	0	85	67	65	91	86	92	81	66	87
0	10	88	65	71	100	92	99	78	89	100
25	10	84	66	71	100	90	97	75	87	100
50	10	84	73	76	100	93	95	89	91	100
75	10	85	71	72	100	94	96	87	88	100

(3) The Effect of Daxad 11

16. It has been suggested that Daxad 11 has a stabilizing effect on S-461 formulations. A series of cloths was prepared to determine whether the same effect was present with S-330 formulations. The cloths contained 75% CP binder, no zinc oxide except as noted, and various percentages of Daxad 11 based on the S-330 content. Table VII gives the results of exposure and storage tests. No evidence appears here to justify the use of Daxad 11 as a stabilizer for S-330.

(4) The Effect of Mixing Chloroamides

17. A difficulty encountered in using S-330 as an impregnite was the loss of efficiency of the compound after weathering. It was proposed to initiate the reaction between weathered S-330 and H vapor by the presence of another, more highly reactive chloroamide. A series of cloths was prepared containing mixtures of S-330 with S-461 and S-145. The cloths were impregnated from standard aqueous systems with 75% CP binder and 10% zinc oxide based on the chloroamide content.

Table VII

The Effect of Daxad 11 as a Stabilizer for S-330 (P-2)

(Data given as per cent of original values)

% Daxad 11	Outdoor, Florida, (May, 1943)								75°C-75% R.H. 96 hrs.	
	Clr				T. S.					
	1 wk	2 wk	3 wk	4 wk	1 wk	2 wk	3 wk	4 wk	Clr	T.S.
5	69	47	42	25	100	90	71	56	55	98
10	72	43	42	24	100	83	66	51	60	100
15	66	38	43	22	94	81	67	45	57	100
20	71	59	46	30	71	65	59	26	50	100
*20 (+10% ZnO)	86	78	81	-	100	100	100	-	89	95

*Micronized S-330

Table VIII

Effect of Added Chloroamides on Stability of S-330 Cloths

(Data given as per cent of original values)

S-330	Added Chloroamide	Outdoor, Washington, (Aug., 1943) Cl+ 1 wk	2 wk	3 wk	4 wk	T.S. 4 wk	75°C-75 R.H. 96 hrs. Cl+	T.S.	110°F-75% R.H. 30 days Cl+	T.S.
P-6	None	105	99	102	93	100	107	100	62	96
P-6	5% S-461	73	73	63	56	100	113	99	89	93
P-6	10 "	81	77	66	53	100	78	100	73	96
P-6	15 "	63	65	52	48	100	92	100	80	86
P-6	10 S-145	79	60	49	49	100	95	100	81	100
P-6	20 "	70	57	52	51	100	93	100	76	100
P-6	30 "	68	51	45	44	100	92	96	74	98

S-330	Added Chloroamide	Outdoor, Washington, (Dec., 1943) Cl+ 1 wk	2 wk	3 wk	4 wk	T.S. 3 wk	75°C-75 R.H. 96 hrs. Cl+	T.S.	110°F-75% R.H. 60 days Cl+	T.S.	120 days Cl+	T.S.
Micronized	None	85	71	72	-	100	94	96	87	-	88	100
"	10% S-461	84	76	64	-	100	91	95	91	-	83	92
"	10% S-145	84	80	62	-	100	94	96	92	-	88	100

The impregnated cloths were subjected to the usual tests to determine the behavior of such mixtures. Table VIII gives the data. The reactivity against H vapor after storage and exposure is reported in a later section.

18. The presence of S-145 up to 30% seemed not to affect the stability characteristics of S-330, nor did S-461 up to 15%. The micronized S-330 showed little adverse effect due to the addition of 10% of other chloroamides.

(5) The Effect of Chloroamide Concentration

19. A test was made to determine what effect the original loading of chloroamide on the cloth would have on stability. Cloth samples were impregnated from a standard aqueous system containing 75% CP binder and 10% zinc oxide, based on the S-330 content. Table IX shows the effect of loading on stability in the accelerated storage test.

Table IX

The Effect of Loading on Stability of S-330 (P-7) Cloths

96 hours at 75°C-75% R.H.

Loading Mg. $Cl^+/cm.^2$	% Cl^+ ret.	Loading Mg. $Cl^+/cm.^2$	% Cl^+ ret.
0.98	100	0.64	94
0.96	97	0.55	93
0.86	98	0.54	91
0.82	93	0.45	89
0.76	101	0.44	96
0.75	102	0.38	90
0.65	95	0.34	94

Table X gives the data on a similar loading series prepared with micronized S-330. Consideration of the data in Tables IX and X leads to the conclusion that no significant effect can be attributed to S-330 loading.

Table X

The Effect of Loading on Stability of Micronized S-330 Cloths
(Data given as percent of Original Values)

	Outdoor Florida, (Dec.,1943)				75°C-75% R.H. 96 hrs.		110°F - 75% R.H.		
	Cl^+			T.S.			Cl^+		T.S.
Mg. $Cl^+/cm.^2$	1 wk	2 wk	3 wk	8 wk	Cl^+	T.S.	60 da	120 da	120 da
0.5	85	69	68	100	87	96	91	86	100
0.7	85	71	73	100	94	96	87	88	100
1.0	87	66	80	100	93	98	78	38	100

(6) The Effect of Stabilizers

20. Several of the tables above include stabilized formulations for direct comparison with the unstabilized. In addition a series of cloth samples was impregnated from a standard aqueous system containing 75% CP binder in which only the amount of stabilizer was varied. The data is given in Table XI. There are no significant differences among different amounts of zinc oxide. The unstabilized and $CaCO_3$ stabilized cloths show a poorer chlorine retention than the zinc oxide cloths in the 110°F tropical storage. The first 10% does make an important difference both in active chlorine retention and tensile strength retention. Table XII gives the data for a similar series for micronized S-330. Here the results are not as clear-cut, due possibly to the superior inherent stability of the micronized material. However, in this case also, the presence of 10% or more of ZnO improves the chlorine retention. 10% $CaCO_3$ stabilizes S-330 only a little less well than 10% ZnO in the outdoor and tropical storage tests.

Table XI

The Effect of Stabilizers on S-330 Impregnated Cloths
(Data given as per cent of original values)

S-330	CP	Stab.	Outdoor, Washington, (August, 1943) Cl⁺ Ret. 1 wk	2 wk	3 wk	4 wk	T.S. Ret. 1 wk	2 wk	3 wk	4 wk	75°C-75 R.H. 96 hrs. Cl	T.S.	110°F-75 R.H. 30 days Cl	T.S.
P-5	-		65	59	50	39	100	99	68	67	89	100	50	100
P-5	-	10% ZnO	87	68	69	53	100	100	100	90	97	100	80	96
P-5	-	25% "	87	82	72	58	100	100	100	91	86	100	82	99
P-8	75	15% ZnO	64	46	44	40				100	114	100	105	100
P-8	75	20% "	81	65	73	55				100	95	100	101	100
P-8	75	25% "	69	62	53	53				100	107	98	93	100
P-6	75	10% $CaCO_3$	75	63	63	46				96	93	100	56	94
P-6	75	25% "	69	56	52	40				95	110	100	41	99

Table XII

The Effect of Stabilizer on the Weathering of Micronized S-330 Cloths
(Data given as per cent of original value retained)

Stabilizer	Outdoor, Florida (Dec., 1943) Cl⁺ ret. 1 wk	2 wk	3 wk	T.S. ret. 1 wk	2 wk	3 wk	96 hr. at 75°C-75% RH Cl⁺	T.S.	110°F-75% RH Cl⁺ 2 mo.	4 mo.	T.S. 4 mo.
0% ZnO	85	67	65	100	100	91	86	92	81	66	87
10% "	85	71	72	100	100	100	94	96	87	89	100
17% "	89	80	68	100	100	100	98	98	92	87	100
25% "	87	85	58	100	100	100	97	97	94	93	100
10% $CaCO_3$	86	81	57	100	98	100	93	95	91	74	96

(7) The Effect of Dyes

21. There is evidence that ultraviolet radiation accelerates the rate of decomposition of chloroamides. However, the pigments used in the standard impregnation formulation apparently slow down the decomposition of S-330 on outdoor weathering. This is shown in Table XIII where, both with and without stabilizer, the presence of dye improved the chlorine retention. The effect is not apparent in the accelerated tests where there is no sunlight.

Table XIII

The effect of Dyes on the Stability of S-330 Cloths
(Data is given as per cent of original value)

S-330	CP	ZnO	Color	Cl⁺ Ret. 1 wk	Cl⁺ Ret. 2 wk	Cl⁺ Ret. 3 wk	Cl⁺ Ret. 4 wk	T.S. Ret. 1 wk	T.S. Ret. 2 wk	T.S. Ret. 3 wk	T.S. Ret. 4 wk	75°C-75 R.H. 96 hrs. Cl⁺	75°C-75 R.H. 96 hrs. T.S.	110°F-75 R.H. 30 days Cl⁺	110°F-75 R.H. 30 days T.S.
P-5	-	-	-	65	59	50	39	100	99	69	67	88	100	50	100
P-5	-	-	khaki	89	80	87	65	100	100	98	92	77	100	58	100
P-5	-	10%	khaki	81	70	73	57	100	100	100	100	97	100	80	100
P-5	-	-	blue	90	63	83	66	100	100	100	85	78	100	35	100
P-5	-	10%	blue	88	99	75	50	100	100	100	100	90	100	79	100
P-1	75%	-	-	*56	40	26	14	95	88	74	54	56	90		
P-1	75	10%	-	*80	64	50	39	100	100	100	87	83	100		
P-2	75	-	blue	*71	71	59	49	100	92	73	55	59	93		
P-2	75	10%	blue	*91	64	71	55	100	100	100	92	78	100		
P-2	75	-	khaki	*71	67	42	24	100	98	98	73	63	100		

*These cloths were weathered in Florida during May, 1943; the others at Washington during June, 1943.

Table XIV

Stability of COF S-330 Cloths

(Data given as per cent of original values)

Impregnite	CP	ZnO	Outdoor Weathering, (Washington, Oct., 1943) Cl⁺ Ret. 1 wk	2 wk	3 wk	4 wk	T.S. Ret. 1 wk	2 wk	3 wk	4 wk	75°C-75 R.H. 96 hrs. Cl⁺	T.S.	110°F-75 R.H. 30 days Cl⁺	T.S.
COF	0	0	79	69	59	52	90	76	70	65	71	93	66	92
COF	25%	0	79	69	57	56	87	75	68	64	74	90	75	88
COF	50	0	70	65	59	49	88	76	64	63	75	91	70	91
COF	75	0	87	72	59	53	94	82	70	65	72	93	63	91
COF	75	10	75	65	53	49	100	96	98	83	87	100	110	99
Micronized	75	10	81	90	79	78	100	98	100	96	106	100	83	90
S-145	75	10	65	61	49	39	100	100	100	100	72	97	79	98

(8) Behavior of COF Cloths on Weathering.

22. A series of cloths prepared by the chlorination on fabric technique was weathered in the usual manner to determine the behavior of this type of cloth. Table XIV gives the data. From outdoor weathering it appears that COF cloths deteriorate a little more rapidly than cloths prepared with micronized S-330, but a little less rapidly than S-145 cloths.

(9) Behavior of Micronized S-330 Cloths on Laundering.

23. Table XV gives data on the laundering of S-330 cloths. The data leads to the following conclusions.

(a) The presence of binder increases the laundering resistance of S-330 cloths considerably. However, the quantity of binder from 25% to 75% appears to make no difference.

(b) S-330 is superior to S-461 in respect to laundering resistance under the same conditions, and is equal to S-145

(c) The loading makes no difference on laundering in the range of 0.5-1.0 mg. $Cl^+/cm.^2$

(d) The presence or absence of ZnO does not effect the laundering resistance to any marked degree.

(e) The presence of 10% S-461 or 10% S-145 does not affect the laundering resistance of S-330.

(f) The laundering resistance of COF formulations is comparable to micronized S-330 formulations.

Table XV

The Laundering Resistance of Micronized S-330 in Various Formulations

Compound	% CP	Stabilizer % ZnO	Other	% Cl^+ retained 90°F, 0.06% Nacconol NR 1 wash	2 wash	3 wash	4 wash	60°C 0.5% Ivory Soap 5 wash
S-330	0	0		57	46	43	38	16
	25	0		93	88	86	84	57
	50	0		89	83	86	85	60
	75	0		89	83	85	81	48
S-330	0	10		56	44	34	32	15
	25	10		78	68	68	70	39
	50	10		86	87	87	85	64
	75	10		84	78	75	77	45
Low Loading S-330	75	10		90	80	76	73	36
High Loading S-330	75	10		86	78	76	75	34
S-330	75	17		92	89	82	82	51
	75	25		94	92	85	88	62
	75	10	$CaCO_3$	94	91	88	88	61
	75	10	10 S-461	85	78	75	79	52
	75	10	10 S-145	89	87	85	85	60
	225	76	58 Daxad	96	96	92	93	69
	225	60	14 Daxad	94	89	83	92	40
COF (S-330)	0	0		88	72	50	45	-
	25	0		94	78	58	53	-
	75	0		96	93	85	89	-
	75	10		96	92	79	77	
S-461	225	75	60 Daxad	55	45	37	28	0
	225	60	15 Daxad + $MnAc_2$	40	24	8	4	0
S-145	75	10		80	72	74	75	43

D. Vesicant Penetration Tests

(1) Comparison of Chloroamides

24. Results of vesicant vapor tests of cloth impregnated with S-330 by the tetrachloroethane solvent process are described in Memorandum to the Director, "The Evaluation of Impregnite S-330," dated 19 November 1942. The data obtained in these tests are reproduced in Tables XVI and XVII.

Table XVI

Vesicant Vapor Penetration Tests on Unweathered Samples

Impregnite	Agent	Protective Time (Min.) by 0.1 mg. $Cl^+/cm.^2$	Protective Time (Min.) by 0.1 mg. S-Cmpd./$cm.^2$	% Cl^+ Remaining After Test
S-145 (DPU)	H	40.7	5.9	2.3
S-145 (TCA)	H	33.8	4.9	9.5
S-328	H	22.5	7.4	50.1
S-330	H	50.6	17.0	0.6
S-461	H	54.0	24.8	12.8
S-145 (DPU)	L	< 3.0	< 0.4	1.8
S-328	L	< 2.5	< 0.8	-
S-330	L	11.4	3.8	13.6
S-145 (DPU) + 25% ZnO	L	6.2	0.9	17.5

Table XVII

Vapor Penetration Tests on Samples after Exposure to 75°C and 75% R.H. for 96 hrs.

Impregnite	Agent	Protective Time (Min.) by 0.1 mg. $Cl^+/cm.^2$	Protective Time (Min.) by 0.1 mg. S-Cmpd./$cm.^2$	% Cl^+ Remaining After Test
S-145 (DPU)	H	38.6	5.6	2.3
S-145 (TCA)	H	30.4	4.4	8.1
S-328	H	3.5	1.1	78.1
S-330	H	52.7	17.4	0.0
S-461	H	53.2	24.5	9.0

It was concluded from the results of these tests that, per unit weight of active chlorine, S-330 has about the same protective capacity toward H vapor as S-461 and greater capacity than S-145

and S-328. It was also shown that S-330 gives some protection against L vapor, whereas other chloroamides do not.

25. Since the above data were reported, it has become evident as the result of gas chamber tests with human subjects that the magnitude of vesicant vapor leakage through the impregnated clothing is of greater physiological significance than the overall protective capacity. In this respect S-330 is markedly inferior to S-145 and S-461, especially after weathering or storage.

26. In chemical penetration tests used in this investigation, the rate of leakage of vesicant vapor is determined by the time required for an indicator bubbler to be discharged. Since each bubbler detects a given amount of vesicant vapor (0.2 mg. of H), short bubbler times indicate a high leakage whereas long bubbler times indicate a low rate of leakage. In particular, a high initial leakage of vesicant vapor is indicated when the first one or two bubblers are discharged in a short time compared to succeeding bubblers. This is illustrated in Table XVIII which shows the discharge times for five successive bubblers

Table XVIII

Initial Vapor Leakage in Penetration Tests

Impregnite	Weathering or Storage	Mg. $Cl^+/cm.^2$	Bubbler Times (Minutes) 1	2	3	4	5
S-145	None	0.358	67.4	39.7	32.0	18.2	10.0
S-328	"	0.564	78.8	69.1	35.9	22.3	17.4
S-330	"	0.474	20.7	96.3	74.6	37.2	20.5
S-461	"	0.506	113.0	68.4	43.2	21.7	18.1
S-145	75°C-75% R.H.	0.326	52.6	50.4	17.4	8.9	7.7
S-328	"	0.354	12.1	10.1	8.4	8.7	8.6
S-330	"	0.457	24.1	33.3	88.9	132.5	21.3
S-461	"	0.412	55.5	92.8	45.1	27.2	19.5

27. The high initial leakage of the S-330 impregnated cloth as compared to S-145 and S-461 is shown by the low first bubbler times. The above data also show the lack of capacity and extremely high leakage characteristic of S-328 impregnations after weathering. These effects are more clearly demonstrated by a graphical presentation of the data in Plates 1 and 2. The curves in these plates show the concentration of H in the effluent air stream during the course of the penetration test.

28. It has been found that aqueous impregnations of S-330 show the same characteristics as solvent impregnations with regard to leakage and capacity. A comparison with S-145 impregnated by the aqueous process is given in Table XIX. In this table the capacity is expressed in terms of protective time (min.) afforded by 0.1 mg. $Cl^+/cm.^2$ and the initial reactivity or leakage is shown by the time required for the first 0.2 mg. H vapor to penetrate the cloth (1st Bubbler Time).

Table XIX

H Vapor Penetration Tests on Samples Impregnated from Aqueous Suspensions

Impregnite	Weathering or Storage	Capacity Min./0.1 mg. $Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (Min.)
S-145	None	76.6	133
S-330	None	69.7	22
S-145	75°C - 75% R.H. (96hrs.)	50.5	112
S-330	"	60.7	22
S-145	Tropical (1 mo.)	71.2	140
S-330	"	63.6	115
S-145	Outdoor, Florida (3 wks)	39.9	100
S-330	"	57.6	19

29. The data in the above table show that in protective capacity S-330 compares very favorably with S-145 when impregnated from an aqueous suspension, but that the initial reactivity is much less. It will be shown later that this initial leakage of H vapor is highly significant physiologically and represents a most important criterion in the evaluation of S-330 for use in protective clothing.

(2) The Effect of Binder Concentration.

30. To determine if the concentration of chlorinated paraffin binder present on cloth impregnated with S-330 had any significant effect on the H vapor penetration properties of the cloth, samples with varying binder concentrations were subjected to standard penetration tests. The results obtained in these tests are given in Table XX.

Table XX

Effect of Binder Concentrations on H Vapor Penetration
Samples Impregnated from Aqueous Suspensions

Binder % CP*	Weathering or Storage	Capacity Min./0.1 mg. $Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (min.)
0	None	51.6	10
25	"	12.1	13
50	"	87.9	22
75	"	24.2	16
0	75°C-75% R.H. (96 hr.)	36.4	7
25	"	63.6	11
50	"	57.5	14
75	"	3.0	14
0	Tropical (1 mo.)	69.7	8
25	"	45.5	10
50	"	89.3	15
75	"	53.0	17
0	Outdoor (3 wks.) at NRL	60.6	11
25	"	45.5	14
50	"	57.6	15
75	"	25.8	19

* % CP is expressed on the basis of the S-330 content.

31. The above data show that the concentration of chlorinated paraffin has no effect upon either the leakage or capacity of the impregnated fabrics. In all cases the initial leakage was high and the capacities were extremely variable.

(3) The Effect of Daxad 11.

32. Although the presence of Daxad showed no stabilizing effect on S-330 impregnations, the series of samples containing various concentrations of this agent was tested for H vapor penetration to determine if any improvement in protection was imparted. Table XXI shows the results of these tests.

Table XXI

Effect of Daxad 11 Concentration on H Vapor Penetration
Samples Impregnated from Aqueous Suspension

Conc. of Daxad 11 (% of S-330)	Weathering or Storage	Capacity Min./0.1 mg. $Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (Min.)
0	None	75.8	41
5	"	63.6	44
10	"	69.7	35
15	"	9.1	35
20	"	81.8	53
0	75°C-75% R.H. (96 hrs.)	94.0	21
5	"	133.0	28
10	"	124.1	28
15	"	54.6	34
20	"	166.6	30
0	Tropical (1 mo.)	64.6	20
5	"	45.5	21
10	"	69.7	27
15	"	98.6	15
20	"	30.6	13
0	Outdoor (3 wks.) in Florida	60.6	23
5	"	42.5	16
10	"	39.4	17
15	"	66.6	18
20	"	36.3	18

33. It may be seen from the data in the foregoing table that the presence of Daxad 11 has no effect upon the penetration characteristics of S-330 impregnations.

(4) The Effect of Mixing Chloroamides

34. Since the high initial leakage of S-330 impregnated clothing represents the most serious disadvantage of this type of clothing, an attempt was made to reduce this leakage by combining S-330 with other, more reactive chloroamides. A series of samples was impregnated with mixtures of S-330 with S-145 and with S-461, and H vapor penetration tests were made. The data are given in Table XXII.

Table XXII

Effect of Mixing Chloroamides with S-330 on H Vapor Penetration
Samples Impregnated from Aqueous Suspensions

S-Compound Added	% of Added S-Compound	Weathering or Storage	Capacity Min./0.1 mg. $Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (Min.)
S-145	10	None	63.2	73
	20	"	101.0	94
	30	"	89.7	118
S-461	5	"	68.3	61
	10	"	91.2	82
	15	"	66.8	60
	33	"	127.0	213
	50	"	63.0	75
	67	"	64.8	263
S-145	10	75°C-75% RH (96 hrs.)	65.7	22
	20	"	99.0	25
	30	"	84.9	28
S-461	5	"	79.3	21
	10	"	64.6	15
	15	"	94.0	25
	33	"	50.9	29
	50	"	37.3	28
	67	"	--	--
S-145	10	Tropical (1 mo.)	--	19
	20	"	--	24
	30	"	--	20
S-461	5	"	--	22
	10	"	--	17
	15	"	--	21
	33	"	--	--
	50	"	--	--
	67	"	--	--
S-145	10	Outdoor (3 wks.) at NRL	55.1	25
	20	"	53.1	30
	30	"	56.9	27
S-461	5	"	32.6	27
	10	"	52.8	24
	15	"	74.5	23
	33	"	58.1	17
	50	"	--	--
	67	"	--	--

35. Mixing more reactive chloroamides with S-330 resulted in a marked decrease in initial leakage of freshly impregnated samples. However, after weathering or storage as indicated, the leakage was as great as in the case of cloth impregnated with S-330 alone. The ratio of concentrations of the chloroamides did not appear to be of any significance.

(5) The Effect of Impregnite Concentration

36. To determine if an extreme variation in impregnite concentration had any effect upon initial leakage of vesicant vapor through S-330 impregnated fabrics, a series of samples with a range of S-330 contents was subjected to H vapor penetration tests, both before and after accelerated storage. The data given in Table XXIII were obtained.

Table XXIII

Effect of Impregnite Concentration on H Vapor Penetration
S-330-Impregnated from Aqueous Suspensions

Conc. of Cl^+ ($mg./cm.^2$)		Initial Reactivity (1st Bubbler-Min.)	
Orig.	After 96 hr. at 75°C-75% R.H.	Original	After 96 hrs. at 75°C-75% R.H.
0.52	0.45	25	23
0.60	0.52	28	21
0.98	0.91	23	23

37. It was concluded from the above data that the impregnite concentration has no effect upon the magnitude of the initial leakage of H vapor through S-330 impregnated clothing.

(6) The Effect of Stabilizers

38. It has been shown previously (NRL Report No. P-2055) that the protective capacity of S-145 is lowered slightly in the presence of ZnO as stabilizer, the decrease being less pronounced in the case of water dispersion impregnations than in the case of solvent impregnations. No difference was observed between 10% and 25% ZnO for either solvent or water impregnations.

39. The effect of ZnO and $CaCO_3$ on S-330 impregnations was evaluated by H vapor penetration tests on a series of cloth samples impregnated with S-330 by the water dispersion process and containing varied concentrations of ZnO or $CaCO_3$. The results of these tests are presented in Table XXIV.

Table XXIV

Effect of Stabilizers on H vapor Penetration
Samples Impregnated from Aqueous Suspensions

Stabilizer	Conc. of Stabilizer (% of S-330)	Weathering or Storage	Capacity Min./0.1 mg.$Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (Min.)
None	--	None	63.3	52
ZnO	10	"	40.9	30
"	15	"	37.9	23
"	20	"	60.6	31
"	25	"	57.6	25
$CaCO_3$	10	"	48.5	29
"	25	"	66.7	28
None	--	75°C-75% RH (96 hr.)	87.9	23
ZnO	10	"	63.6	26
"	15	"	91.0	22
"	20	"	44.0	22
"	25	"	100.0	27
$CaCO_3$	10	"	75.8	21
"	25	"	81.8	18
None	--	Tropical (1 mo.)	--	22
ZnO	10	"	--	16
"	15	"	--	20
"	20	"	--	21
"	25	"	--	23
$CaCO_3$	10	"	--	15
"	25	"	--	16
None	-	Outdoor (3 wks.) at NRL	3.0	19
ZnO	10	"	3.0	18
"	15	"	--	--
"	20	"	3.0	18
"	25	"	3.0	18
$CaCO_3$	10	"	27.3	17
"	25	"	6.1	17

40. The above data indicate that no significant change in either initial reactivity or capacity is produced by the presence of ZnO or $CaCO_3$. It is interesting to note that in this particular series both efficiency and capacity of all samples were greatly lowered by outdoor weathering.

(7) The Effect of Dyes

41. No evidence has ever been obtained that any of the dyes used in S-145 impregnated protective clothing have had any effect upon the vesicant resistance properties of the clothing. That this is also true of S-330 impregnations was shown by a series of penetration tests, the results of which are given in Table XXV.

Table XXV

Effect of Dyes on H Vapor Penetration

Dye	Weathering or Storage	Capacity Min./0.1 mg. $Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (Min.)
None	None	69.7	22
Blue	"	85.0	35
Khaki	"	66.7	46
None	75°C-75% R.H. (96 hrs.)	60.7	22
Blue	"	78.8	23
Khaki	"	48.5	19
None	Tropical (1 mo.)	63.6	15
Blue	"	34.9	16
Khaki	"	63.7	24
None	Outdoor (3 wks.) in Florida	57.6	19
Blue		57.6	26
Khaki	"	63.7	20

(8) The Effect of Particle Size

42. It has previously been shown (NRL Report No. P-2055) that particle size is a determining factor in the protective capacity of S-145 impregnated fabrics, a drop in capacity occurring if the particle size exceeds 15 microns. To evaluate this effect for S-330 impregnations a series of samples impregnated from a water system with S-330 which had been carefully fractionated into particle size ranges was subjected to H penetration tests. The results of these tests are shown in Table XXVI.

Table XXVI

Effect of Particle Size on H Vapor Penetration

Particle Size (Microns)	Weathering or Storage	Capacity Min./0.1 mg. $Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (Min.)
1-5	None	87.9	33
5-10	"	51.5	42
10-20	"	63.6	53
20-30	"	60.6	77
30-40	"	51.5	75
Mixed	"	94.0	25
1-5	75°C-75% R.H. (96 hrs.)	78.8	27
5-10	"	80.4	27
10-20	"	98.5	37
20-30	"	74.3	30
30-40	"	42.4	22
Mixed	"	43.9	20
1-5	Tropical (1 mo.)	--	21
5-10	"	--	24
10-20	"	--	26
20-30	"	--	24
30-40	"	--	24
Mixed	"	--	22
1-5	Outdoor (3 wks.) at NRL	106.1	27
5-10	"	103.0	20
10-20	"	94.0	20
20-30	"	63.6	23
30-40	"	72.7	30
Mixed	"	--	--

43. The data in Table XXVI do not indicate any significant differences as regards particle size of the S-330. The initial leakage in all cases is high, particularly after the weathering and storage treatments.

(9) The Effect of Chlorination on Fabric

44. A number of samples of cloth prepared by the "chlorination on fabric" technique previously described were evaluated for initial leakage of H vapor, both before and after weathering and storage tests. It was hoped that this means of impregnation, which produces a more thorough distribution of impregnite throughout the body of the cloth, would reduce the high initial leakage

characteristic of standard methods of impregnation. The data in Table XXVII are representative of that obtained in testing these samples.

Table XXVII

Effect of Chlorination on Fabric on H Vapor Penetration

Binder	Stabilizer	Weathering or Storage	Capacity Min./0.1 mg. $Cl^+/cm.^2$	Initial Reactivity 1st Bubbler Time (Mins.)
None	None	None	66.6	195
5% CP	"	"	66.6	253
10% CP	"	"	90.9	327
5% CP	"	"	57.6	252
5% CP	10% ZnO	"	54.5	199
None	None	75°C-75% R.H. (96 hrs.)	3.0	17
5% CP	"	"	3.0	14
10% CP	"	"	3.0	22
5% CP	"	"	3.0	24
5% CP	10% ZnO	"	-	-
None	None	Tropical (1 mo.)	-	15
5% CP	"	"	-	19
10% CP	"	"	-	16
5% CP	"	"	-	16
5% CP	10% ZnO	"	-	23
None	None	Outdoor (3 wks) at NRL	81.1	87
5% CP	"	"	93.9	215
10% CP	"	"	63.6	176
5% CP	"	"	60.6	159
5% CP	10% ZnO	"	54.5	140

45. It is evident as a result of this data that the "Chlorination on fabric" technique results in a very satisfactory low initial leakage on exposure of freshly impregnated fabrics to H vapor. Samples after 3 weeks outdoor weathering also exhibited low initial leakage and normal capacity. However, both tropical storage and accelerated storage (75°C-75% R.H.) resulted in a lowered capacity and a high initial leakage.

(10) The Effect of Laundering

46. Since the "chlorination on fabric" method of impregnation resulted in a marked improvement of the protective characteristic of all samples except those exposed to tropical and accelerated

storage, a test was made to determine if laundering of these latter samples would result in improved leakage characteristics. The results obtained are given in Table XXVIII.

Table XXVIII

Effect of Laundering on H Vapor Penetration
Samples prepared by Chlorination on Fabric

Binder	Stabilizer	Weathering or Storage	Initial Reactivity 1st Bubbler Time (Min.)
None	None	Fresh Samples	75
25% CP	"	(Laundered)	215
50% CP	"	"	176
75% CP	"	"	159
75% CP	10% ZnO	"	140
None	None	75°C-75% R.H. (96 hr.)	10
25% CP	"	(Samples Laundered)	20
50% CP	"	"	16
75% CP	"	"	27
75% CP	10% ZnO	"	17

47. No beneficial effect was produced by laundering. The laundered freshly impregnated samples had a low initial leakage but the laundered accelerated storage samples permitted a high initial leakage.

(11) The Effect of Acid Rinsing

48. It was believed that the increased initial leakage of "chlorination on fabric" samples after tropical or accelerated storage might be caused by a covering of the S-330 particles with an inert coating of S-330 base resulting from decomposition of some S-330 during the storage. If such were the case, it was considered theoretically possible to remove this coating by rinsing the cloth in a dilute solution of HCl and thus restore its original good protective characteristics.

49. Accordingly the samples described in Section (9) which showed high leakage after accelerated storage were rinsed first in dilute HCl and then in water. After drying, penetration tests were made and the following data obtained.

Table XXIX

Effect of Acid Rinsing on H Vapor Penetration
Chlorination on Fabric Samples Subjected to Accelerated Storage

Binder	Stabilizer	Initial Reactivity (1st Bubbler Time-Min.) After 96 hr. at 75°C - 75% R.H.	Initial Reactivity (1st Bubbler Time-Min.) After 96 hr. at 75°C-75% R.H. and Dilute HCl Rinse
None	None	17	14
25% CP	"	14	20
50% CP	"	22	15
75% CP	"	24	35

50. The data in the above table show that an acid rinse did not restore the original effectiveness of the "chlorination on fabric" type impregnations.

(12) Summary

51. As a result of the vesicant vapor penetration tests described in this section, the following general conclusions may be made:

(a) Clothing impregnated with S-330 by either the tetrachloroethane solvent process or the aqueous suspension process shows adequate capacity toward H vapor penetration but permits a high initial leakage of vapor both in the case of freshly impregnated samples and samples subjected to accelerated or tropical storage and outdoor weathering.

(b) Clothing impregnated with S-330 by the "chlorination on fabric" process shows adequate protective capacity and does not permit a high initial leakage of vapor in the case of freshly impregnated samples or samples subjected to outdoor weathering. However, such samples subjected to tropical or accelerated storage do permit a high initial leakage of vapor.

(c) Laundering or acid rinsing of "chlorination on fabric" samples after tropical or accelerated storage does not restore the original low initial leakage characteristics of the cloth.

(d) Binder concentration, the presence of Daxad 11, impregnite concentration or particle size, the presence of ZnO or $CaCO_3$, or the presence of dyes do not affect the vapor resistance properties of S-330 impregnated fabrics.

(e) Mixing S-330 with other more reactive chloroamides (S-145 or S-461) results in an improvement in the magnitude of initial ~~leakage~~ of H vapor through freshly impregnated clothing but still allows a high initial leakage after tropical or accelerated storage and outdoor weathering.

E. Physiological Evaluation of S-330

52. To determine the physiological significance of the high initial leakage shown by S-330 impregnated clothing in chemical penetration tests, a series of "arm-chamber" tests was made in the arm-chamber. The design and operation of this chamber are described in NRL Report No. ~~P-2219~~, "~~Chamber~~ Tests with Human Subjects, Part III, Design, Operation and Calibration of a Chamber for Exposing Forearms to H Vapor." Three types of clothing were tested in this series:

(a) Standard S-145 aqueous process impregnated clothing, freshly prepared.

(b) S-330 aqueous process impregnated clothing, freshly prepared.

(c) S-330 aqueous process impregnated clothing, stored at 75°C-75% R.H. for 96 hours.

53. The clothing consisted of full-length Arnzen cloth sleeves. These sleeves were worn by the subjects underneath a standard S-145 impregnated protective jumper. ~~In dressing the~~ subjects, standard wool, impregnated gloves were pulled over the sleeve to be tested, rolled back to the wrist and taped. The sleeves of the jumper were rolled back and taped so that a 3" strip of the sleeve to be tested was left uncovered.

54. The arms of the subjects dressed as described were exposed to H vapor in the arm chamber under the following conditions:

Temperature and humidity:	90°F - 65% R.H.
Concentration of H vapor:	20 γ H/l.
Time of Exposure :	1 hour
CT (mg. min./m.^{3}) :	1200
Number of exposures :	1

55. The clothing was worn for 4 hours after the exposure, and readings were taken at 24 and 48 hours.

56. The results of this test are presented in the following table.

Table XXX

Physiological Evaluation of S-330

Type of Cloth	No. of Arms	Reaction 24 hours	48 hours
Fresh S-145	3	E-?	--
		0	--
		0	--
Fresh S-330	3	E-	E-
		E-	E-
		E-	E-
S-330 after 96 hrs. at 75°C-75% R. H.	3	E	E+
		E	E+
		E-	E+

Legend: 0 = No reaction E = Moderate erythema
E-? = Trace E+ = Papular erythema
E- = Mild erythema V = Vesicle

57. The data in the above table show quite clearly that the S-330 impregnations are physiologically inferior to the S-145 impregnation. The aged S-330 clothing was much less efficient than the freshly impregnated cloth.

58. That the physiological differences of the three types of clothing is a function of the degree of initial leakage as observed intthe chemical penetration tests is indicated by a comparison of the data obtained in penetration tests of samples from the same sleeves tested in the chamber. The data are given in Table XXXI.

Table XXXI

H Vapor Penetration Tests on Sleeves Used in Arm Chamber

Type of Cloth	Initial Reactivity 1st Bubbler (Min.)
Fresh S-145	130
Fresh S-330	34
S-330 after 96 hours at 75°C-75% R.H.	16

59. As a result of the above tests, initial leakage as indicated by the chemical penetration test appears to be physiologically significant, and the high initial leakage of S-330 impregnated clothing represents a serious consideration in the use of this compound for protective clothing.

SUMMARY AND CONCLUSIONS

1. The compound S-330 has been investigated as an impregnite for permeable protective clothing. The use of S-330 in formulation of aqueous impregnating systems has been studied in the laboratory and in a portable impregnating plant. The results showed that S-330 could be satisfactorily formulated and was in this respect comparable to the present impregnite S-145.

2. A novel method of applying impregnite to cloth has been developed which utilizes the solubility of unchlorinated S-330 in dilute acid. Application of a water solution of S-330 base to cloth followed by exposure to chlorine gas results in an impregnated fabric which is soft, pliable, and does not dust.

3. Cloth samples were impregnated with several different chloroamides and compared as to retention of active chlorine and tensile strength upon storage and weathering. The compound S-330 was superior or equal in stability to S-145, S-328, S-461, and S-222.

4. Several series of impregnations were carried out in which the different components of the impregnating bath were used in various amounts. Active chlorine and tensile strength retention were not greatly affected for S-330 impregnated cloths when any of the following components were varied: the binder, chlorinated paraffin; the stabilizers, ZnO or $CaCO_3$; the dispersing agent, Daxad 11; or the water dispersible dyes. Addition of other chloroamides had very little effect of stability on S-330 impregnated cloth samples. S-330 impregnated fabrics prepared by the chlorination on fabric procedure were less stable on outdoor exposure than normal samples.

5. A comparison of the laundering resistance of various S-330 impregnated fabrics revealed that lack of a binder results in poor resistance to laundering.

6. A comprehensive series of vesicant vapor penetration tests have been carried out on S-330 impregnated cloth samples. The capacity of S-330 on fabric for destroying mustard gas is excellent in comparison with the chloroamide S-145. However, there are marked differences in initial leakage of H vapor. S-330 cloth samples, especially after storage or outdoor exposure, show a high initial leakage of H whereas S-145 cloths show very little initial leakage.

7. Variations in the amount of binder, stabilizer, Daxad 11, dyes, and in impregnite particle size on S-330 cloth samples were investigated from the standpoint of H penetration. No significant

effects were found inasmuch as all samples still exhibited a high initial leakage especially after storage or weathering.

8. Addition of other more reactive chloroamides to S-330 in an effort to minimize initial H leakage resulted in an improvement for unaged cloth samples. After storage or weathering, however, the cloth samples impregnated with mixed chloroamides exhibited the high initial leakage characteristic of S-330.

9. Very low initial leakage of H vapor was found for cloth samples prepared by the chlorination on fabric technique. No increase in initial leakage occurred after outdoor weathering. However, tropical storage and accelerated storage tests resulted in high initial leakage.

10. Laundering or acid-rinsing of aged samples of cloth impregnated with S-330 failed to improve the high initial leakage characteristics of S-330.

11. The physiological significance of the high initial leakage observed in chemical penetration tests was determined in a series of "Arm-chamber" tests. Subjects wearing S-330 impregnated sleeves which had been aged for 96 hours at 75°C-75% R.H. exhibited severe erythema after one exposure to H vapor at a CT of 1200.

12. Consideration of all the data leads to the conclusion that S-330 is an excellent compound from the standpoint of stability upon storage or weathering but cannot be considered as an impregnite because of its failure to prevent leakage of H vapor through clothing impregnated by methods now known.

RECOMMENDATIONS

1. It is recommended that S-330 not be used as an impregnite for permeable protective clothing because of leakage of H vapor through such impregnated clothing.

2. It is recommended that further investigation be made in an effort to improve the protective value of S-330 because of its otherwise outstanding properties in regard to stability, non-irritancy, protection against Lewisite, and lack of degrading action on cotton fabric.