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Report on

The Evaluation of Activated Carbon as an Anti-vesicant Agent in Protective Clothing

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ABSTRACT

This report describes a series of tests made with protective clothing containing activated carbon. It is intended as a progress report since several of the problems are still under active investigation.

Results are reported on the effect of weathering, laundering, and wearing trials on several types of carbon cloth. Particular emphasis is placed on a study of the desorption of vesicant from contaminated cloth and on methods of reactivation of the poisoned carbon.

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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. These investigations were undertaken as a continued evaluation of activated carbon as an anti-vesicant agent in protective clothing. The behavior and properties of cloth containing activated carbon that were deemed most important for this study include the following: (1) the effect of storage and weathering, (2) the effect of various laundering agents, (3) the measurement and prevention of desorption of vesicants, (4) reactivation of poisoned carbon and, (5) the effect of wearing.

KNOWN FACTS BEARING ON THE PROBLEM

3. Protective garments made from cloth containing finely divided activated carbon were first developed by the British as a method of protecting the human body against the vapors of all vesicants. This represents a unique method of protection since vesicant gases are absorbed but not neutralized by chemical reaction as is the case with chloroamide impregnated clothing. The principal problem proposed by the British was the search for a substitute for rubber latex which is the binder in their method of impregnation. Preliminary experiments along this line were carried out at this Laboratory in the spring and summer of 1942. The NDRC then undertook extensive research and development work, and, as a result, three different types of protective fabric have been proposed for consideration. The types may be listed in terms of the method of incorporation of the carbon:

1. Coated
2. Impregnated
3. Incorporated directly in synthetic fibers.

4. Numerous patch tests conducted by the CWS, the NDRC, and this Laboratory have demonstrated the importance of desorption of vesicant vapors from cloth containing activated carbon. These tests have shown that a physically significant desorption may occur when a fabric has absorbed only 10% of its total capacity for H vapor. Thus the total capacity of a fabric containing activated carbon has little meaning. This was further demonstrated in chamber tests at this Laboratory wherein worn garments of much lower total capacity were found to give protection equivalent to unworn garments of high total capacity.

THEORETICAL CONSIDERATIONS

5. A large amount of research work has been done during the past three years on the protective value of permeable protective clothing. Some correlations have become apparent between laboratory penetration tests and chamber tests with human subjects. For example, the protection afforded by a single layer of clothing impregnated with a chloroamide has been found to depend more upon efficiency of vesicant agent removal than the total capacity. Hence, laboratory tests which evaluate only the capacity of a fabric have much less meaning than one which measures the efficiency.

6. The consideration of activated carbon as an anti-vesicant agent in protective clothing brings forth another factor, namely, the desorption of vesicant agents from contaminated fabric. Efficiency of vesicant agent removal is still important since little protection can be expected from a fabric that permits a high leakage of vesicant vapors. The total capacity is probably as important for carbon treated clothing as it is for chloroamide treated clothing from the standpoint of representing a reservoir of protective value against mechanical loss through wear and laundering.

7. Unfortunately, no satisfactory laboratory method has yet been found to test carbon treated fabric for rate of desorption of vesicants. Without such a laboratory method recourse must be had to patch tests on human subjects. Since evidence already exists that the efficiency of carbon tested clothing is adequate, the desorption factor becomes the most important one to consider. Great improvement in protective value would result if the desorption rate for activated carbon was not appreciable until a larger fraction of the full capacity was reached.

PREVIOUS WORK DONE AT THIS LABORATORY

8. Previous work done on weathering, laundering and reactivation of carbon cloths is contained in a Memorandum to the Director, "Testing of Carbon Coated Cloths Submitted by Dr. Dana Burks, Jr., of the Slatersville Finishing Company," dated March 8, 1943. Although only the coated type of fabric was tested, considerable data was acquired on the problems of weathering, laundering, and reactivation. It was found that ordinary soaps and detergents could not be used for laundering cloth coated with activated carbon, as these soaps thoroughly poisoned the activated carbon. In no case was weathering alone found to have significantly adverse effects on the activity of the carbon. The sole effect of the weatherings was to cause a deterioration of the binders used to hold the carbon on the cloth, thus decreasing the crocking resistance of the coated surfaces. There were also indications

that varying degrees of reactivation of poisened cloths could be attained with water and with certain dry cleaning agents.

9. NRL Report No. P-2239 entitled "Chamber Tests with Human Subjects, IV. Tests on Carbon Clothing." describes the results of chamber tests run with H vapor on suits prepared from carbon coated cloth, as well as the results of patch tests made with different cloths, vesicants, amounts of vesicant, and methods of application. The data and results given in that report have been used in the present report in substantiation of various conclusions.

EXPERIMENTAL PART

I. Storage and Weathering

A. Outdoor Weathering

10. Samples of the three different types of cloth containing activated carbon were subjected to outdoor exposure both in Washington and in Florida. The samples tested were: (1) NDRC March Model (coated cloth); (2) NDRC May Model #1 (impregnated cloth); and (3) Costa April Model (a two-ply cloth of cotton and carbon-containing viscose rayon fibers). The samples were exposed during the months of May to November, 1943 on 45° angle racks facing south. Each month, for 6 months, samples were tested for crocking resistance and for total capacity for H vapor as measured by the method described in NRL Report No. P-1831. Crocking of the NDRC March and NDRC May Models became progressively worse during the test. The binder used in the impregnation of the NDRC May Model deteriorated to such an extent after 3-4 month's exposure that much of the carbon could be removed from the cloth by moderate rubbing or shaking. The carbon-rayon fibers of the Costa Cloth did not deteriorate noticeably.

11. The results of the vesicant penetration tests, though somewhat erratic, show that the activity of the carbon is not appreciably decreased by exposure to outdoor weathering conditions except for the NDRC May Model. The decrease in penetration time for the NDRC March and NDRC May Models may be ascribed to the loss of carbon upon deterioration of the binders used. The unusual increase in penetration time shown by the Costa Model can only be explained by a noticeable shrinkage of the cloth during exposure.

A summary of vesicant penetration times is given in Table I.

Table I

H Penetration Times of Carbon Cloths After Outdoor Exposure

Exposure	NDRC March Model (Wash.)	NDRC March Model (Florida)	Costa Model (Wash.)	Costa Model (Florida)	NDRC May Model (Wash.)
Original value	411 min.		572 min.		410 min.
1 month	238	264	578	299	242
2 months	148	270	286	264	324
3 months	207	243	580	475	-
4 months	227	216	590	483	327
5 months	290	272	547	519	107
6 months	266	275	778	651	-

B. Storage Tests

12. Under actual conditions where suits made from carbon cloth might be worn, it is probable that undergarments might be treated with standard chloroamide impregnite. Consequently, storage tests were made to determine the effect of the chloroamide on the activated carbon. Swatches of NDRC March Model and Costa Model carbon cloth were rolled in intimate contact with swatches of standard solvent and aqueous impregnated Arnzen Cloth. These rolls of cloth were storad at room temperature and under simulated tropical storage conditions of 110°F and 75% relative humidity for a 6 months period. H penetration tests after the storage gave the results listed in Table II. Storage at room temperature showed the chloroamide cloths to have little or no effect on the protective capacity of the carbon cloths, while the accelerated storage did cause some apparent deterieration of the NDRC March Model Cloth.

Table II

H Penetration Times of Carbon Cloths Stored with Chloroamide Cloths

Storage Conditions	Penetration Time NDRC March Model	Costa Model
Original Value	411 min.	572 min.
6 mo. 110°F/75% RH	277 min.	-
6 mo. 110°F/75% RH + solvent chloroamide cloth	64 min.	270 min.
6 mo. 110°F/75% RH + aqueous chloroamide cloth	30 min.	700 min.
6 mo. room temperature + solvent chloroamide cloth	350 min.	545 min.
6 mo. room temperature + aqueous chloroamide cloth	336 min.	429 min.

II. Desorption of Vesicant From Contaminated Cloth

A. Determination and Measurement of Vesicant Desorption

(1) Physiological Tests

13. Patch tests on men were first used as the most reliable and convenient method of evaluating the desorption of vesicant. It was possible in this type of test to use a wide range of contamination levels.

14. The NDRC March Model carbon-coated cloth used contained 5.35 mg. carbon/cm.^{2} and had a chemical break-time of 411 minutes. Samples of the cloth were contaminated by exposure of the uncoated side to saturated H vapor at 30°C in the cups used for penetration tests. The method used for determining the concentration of H on the exposed cloth consisted of extraction with hot 20% acetic acid followed by potentiometric titration with standard NaOCl solution. The amount of H absorbed at various exposure times is given in Table III.

Table III

H Absorbed by Carbon-coated Cloth at Various Exposure Times

Exposure Time (min.)	Mg. H/cm.^{2}
5	0.015
10	0.030
30	0.095
50	0.155
100	0.310

15. The physiological tests were carried out as described in NRL Report P-2239. The samples of contaminated cloth were applied to the forearm with the unexposed side next to the skin. The samples were 1-centimeter square and were secured and covered by a 1-inch strip of adhesive tape.

16. In one test using ten men the contaminated patches were worn for four hours. The room temperature during the wearing period was 85°F and the relative humidity was 75%. Readings were taken at 48 hours. The results are given in Table IV.

Table IV

Patch Tests of Contaminated NDRC March Model Cloth

H exposure time (min.)	Results (48 hour readings) 0	E-?	E-	E	E+	V
5	4	6				
10		5	5			
30		2	2	5	1	
50			1		5	4
100						10

Legend:
- 0 = no reaction
- E-? = trace
- E- = faint to mild erythema
- E° = mild to moderate erythema
- E = moderate erythema
- E+ = raised erythema
- NPV = numerous pin point vesicles
- V = vesicle

17. From Table IV, the severity of this desorption can easily be ascertained. The carbon cloth samples, exposed to only 25% of their total H capacity produced vesication in all cases.

18. To determine the relative importance of the time of wearing a test was run in which the time of wearing was varied from 1 to 4 hours. Carbon coated cloth samples were exposed to H vapor for thirty and fifty minutes and applied as before, using five men in each group. The temperature was 87°F and the relative humidity was 55%. Readings were taken at 48 hours. The results are given in Table V.

Table V

Effect of Wearing Time

H Exposure time (min.)	Wearing time (hrs.)	Results (48 hours) 0	E-?	E-	E	E+	V
30	1		1	4			
	2			2	2	1	
	3				5		
	4				2	2	1
50	1		1	1	1		2
	2				1		4
	3				1		4
	4				1		4

19. It can be seen from Table V that the more highly contaminated cloth caused more severe burns regardless of wearing time, and that a longer period of wear produced a more severe burn.

20. From Tables IV and V, it is readily apparent that there is a marked desorption of vesicant vapors from carbon coated cloth that has been exposed to H vapor for less than 10% of its total capacity. Of course, the conditions of wear used (direct contact with the skin and covered) are the most severe that could be expected in the actual wear of suits made from this type cloth. NRL Report P-2239 reports the results of an extensive investigation of other methods of testing this desorption effect, using the same type samples of cloth separated from the skin by underwear cloth, by an air space alone, and by air space and underwear cloth. As might logically be expected, the burns received from the less harsh applications are less severe. However, the reactions were still marked and gave conclusive evidence that the desorption effect was still dangerous in these cases.

(2) Laboratory Tests

21. The desirability of having a reliable laboratory test for the desorption of vesicant vapor is evident in that it would provide a quick, harmless method of determining the relative degree of danger of samples of contaminated carbon cloths. Several methods of testing for vesicant desorption were tried,

such as the use of Spotted Dick Papers, DB-3 test papers, and DB-3 tubes.

22. The first series of tests attempted to apply the Spotted Dick Test because of the ease and speed of the test. A description of the Spotted Dick Test may be found in NRL Report P-2065. In the testing of the contaminated carbon cloth samples, the Spotted Dick Test papers were always applied to the side of the cloth which was not exposed to the H vapors. Primarily, efforts were made to obtain test results which would give a correlation between these tests and the known physiological test results. Consequently, samples of the NDRC March Model coated cloth were prepared as previously described with identical exposure times to H vapor. The resulting samples were tested at 35°C and low relative humidity with freshly prepared Spotted Dick Papers. The tests were completely negative except a questionable test over one hour with the cloth exposed for 100 minutes to H vapor. No correlation could be obtained. Contaminated cloths known to be physiologically dangerous did not give a Spotted Dick Test. The use of higher temperatures did produce more rapid test times, but the results were not reproducible. At temperatures of 60 - 70°C, quite rapid tests were obtained with cloths exposed to H vapor for 50 minutes or more. Tests were not obtainable from cloths exposed to less than 50 minutes H vapor because of the short life of the Spotted Dick Test papers at the elevated temperatures. The use of high humidity at the high temperatures further speeded up the tests, but not in a significant manner. The tests were still unreliable.

23. The attempted use of test papers spotted with DB-3 reagent (see NRL Report P-2065) gave even less conclusive results than the Spotted Dick Test papers.

24. The use of DB-3 Tubes was next attempted. The DB-3 Tubes consisted of small glass tubes filled with silica gel on which DB-3 reagent had been impregnated. Contaminated air was drawn through the tubes, any H vapor absorbed on the silica gel, and then made to react with the DB-3 reagent by heating to 100°C for a minute or two. Addition of a drop of dilute NaOH solution after heating caused a blue color to appear if vesicant vapor had been absorbed. The width of the color band developed was taken as a direct measure of the amount of vesicant vapor absorbed.

25. In the first attempt to obtain a test with the DB-3 tubes an inverted funnel was placed over the contaminated cloth sample for varying periods of time, and a DB-3 tube was attached to the upper end of the inverted funnel. After the period of standing, the air in the funnel was aspirated through

the DB-3 tube and the reagent developed as described. At room temperature no test was obtained from physiologically dangerous samples after standing periods up to 16 hours. Next, a method was tried in which dry air (50 cc./min.) was continuously aspirated over the surface of the contaminated sample and then through a DB-3 tube for periods of time up to four hours.

26. Negative results were obtained with this method. The use of saturated air instead of relatively any air in the aspiration method produced a few tests which, as in other methods, were not reproducible.

27. These results led to the conclusion that patch tests were the only satisfactory method of detecting and measuring the desorption of vesicant vapors from contaminated carbon cloth. However further investigations are being conducted to find a suitable laboratory test.

B. Prevention of Desorption

28. It was thought possible to prevent desorption of vesicants from contaminated carbon in two ways. One would be to destroy the vesicant chemically and the other would be to increase the adsorption bond to such an extent that no desorption would occur. Methods were employed to prevent desorption which could act in either of these two ways.

(1) Use of Special Carbons

29. All carbon cloth previously made contained only one type of activated carbon, CWS-N 44. It has been considered possible that other base carbons or some type of chemically impregnated carbon might show either or both of the desirable properties discussed above. In addition to the CWS-N 44 carbon, which is made from wood flour, MSA-G_1, a coconut base carbon, and PCI-Pn-1, a coal base carbon were chosen as representative of the different types of activated carbons. In addition to these base carbons, chemically impregnated types of each were also used. Table VI contains a list of the different carbons used.

Table VI

Carbon Samples Tested

Designation	Description
N-44 Base	$ZnCl_2$ activated wood flour (used in all previous tests)
N-44 Type ASC	N-44 Base chemically impregnated with salts of Cu, Ag, and Cr.
MSA-G_1 Base	Activated coconut charcoal
MSA-G_1 Type ASC	MSA-G_1 Base chemically impregnated with salts of Cu, Ag, and Cr.
PCI-Pn-1 Base	Activated coal charcoal
PCI-Pn-1 Type ASC	PCI-Pn-1 Base chemically impregnated with salts of Cu, Ag, and Cr.
PCI-Pn-1 Type ASM	PCI-Pn-1 Base chemically impregnated with salts of Cu, Ag, and Mo.

30. The seven types of activated carbon were ball milled until the particle size of each batch was less than 5 microns. The resulting ground carbons were then impregnated into Arnzen type DN cloth using the Rohm and Haas method (dispersion of the carbon in an ammonium alginate solution, padding the cloth in the dispersion, scrubbing to remove loose surface particles and a post coating with an emulsion of Rhoplex WC-9). The impregnated cloths were subjected to H penetration tests to determine total H capacity and were analyzed for carbon content. The results of these analyses, and the calculated protective capacities per mg. of carbon for each type carbon are listed in Table VII.

Table VII

Properties of Impregnated Carbon Cloths

Carbon Cloth	Chemical Break Time	Mg. C/cm.^{2}	Min. Protection by 1 mg. C/cm.^{2}
NDRC March Model (N-44 Base)	411 minutes	5.35	75
N-44 Base	370 "	5.07	73
N-44 Type ASC	385 "	4.19	92
MSA-G_1 Base	242 "	5.44	45
MSA-G_1 Type ASC	138 "	4.86	28
PCI-Pn-1 Base	173 "	4.88	35
PCI-Pn-1 Type ASC	211 "	5.09	41
PCI-Pn-1 Type ASM	263 "	6.32	42

31. From the calculated unit protective capacities listed in Table VII, it appears that the MSA-G_1 and PCI-Pn-1 carbons are not as highly activated at the N-44. Except in the one case of the MSA-G_1 Type ASC, chemical impregnation of the carbon itself did not seem to have any adverse effect on the protective capacity.

32. Patch tests were run with each of the different carbons in the manner previously described. One-quarter inch squares of cloths exposed for 10, 30, 50, and 100 minutes to H vapor in the penetration cups were worn covered with adhesive tape for four hours, the unexposed side of the cloth next to the skin. Five men were used in each group. The temperature was 84°F and the relative humidity 40%. The results of the test are given in Table VIII.

Table VIII

Patch Tests with Cloth Containing Different Type Carbons

Cloth	H Exposure time (min.)	Results (48 hours) 0	E-	E	E+	V
NDRC March Model						
N-44 Base Control	10	5				
	30	4	1			
	50	4	1			
	100					5
N-44 Base	10	5				
	30	4	1			
	50	4	1			
	100			1	2	2
N-44 Type ASC	10	5				
	30	5				
	50	4		1		
	100					5
MSA-G_1 Base	10	5				
	30	5				
	50	4	1			
	100				2	3
MSA-G_1 Type ASC	10	5				
	30*	2	1	1		
	50	3	2			
	100		1	2	1	1
PCI-Pn-1 Base	10	4	1			
	30*	1		3		
	50	1		1	3	
	100			1		4
PCI-Pn-1 Type ASC	10	5				
	30*		1	3		
	50	2	1	2		
	100		1		1	3
PCI-Pn-1 Type ASM	10	5				
	30*	2	2			
	50	3	1	1		
	100			2		3

*Fifth man was not read on account of illness.

33. It can be seen from the data in Table VIII that there are no significant differences in the action of the different type carbons used in the test cloths. A positive desorption is evidenced in all cases for those samples exposed to H vapor for 50 and 100 minutes.

34. The cloths giving the results listed in Table VIII were exposed to H vapor 24 hours before the patches were applied. Similar samples aged for 72 hours before application were tested in parallel with the tabulated 24-hour samples, using the other arm. It was hoped that the 3 day aging period might bring about hydrolysis or destruction of some of the H and thus prevent the adverse physiological effects. However, the difference between the results was so slight that Table VIII could apply almost identically. There appeared to be no measurable hydrolysis or desorption of the H in the three day period, even in the presence of certain catalysts.

35. NRL Report P-2239 described a similar test with NDRC March Model cloth applied immediately, aged 3 days in an envelope, and aged 3 days hanging free in a ventilated hood. This test also showed that there was little or no hydrolysis or desorption of H under those conditions.

(2) Effect of Different Types of Cloth

36. Since the protection against vesicants may vary with the method of application of carbon, it was considered possible to cause a difference in the rate of desorption from different type cloths. Four different types of carbon cloth were tested: (1) Coated cloth, NDRC March Model, (2) Impregnated cloth, NDRC May Model, (3) carbon-containing viscose rayon, Costa Model (rayon-cotton 2-ply), and (4) Vinyon fiber containing carbon, Carbide and Carbon Company.

37. Samples of each of the four types of carbon cloth were exposed to H vapor for varying lengths of time, as previously described, cut into squares and tested in direct contact, covered. The patches were worn for four hours by 10 men in each group. The temperature was 87°F and the relative humidity 55%. Readings were taken at 48 hours. The results are given in Table IX.

Table IX

Effect of Type of Carbon Cloth

Cloth	H Exposure time (min.)	Results (48 hours) 0	E-?	E-	E	E+	V
Coated	5		1	9			
	10		2	8			
	30			1	5	2	2
	50					1	9
Impregnated	5		3	7			
	10		3	7			
	30			2	2	6	
	50				2	4	4
Rayon	5	1	3	6			
	10		1	8	1		
	30			1	4	4	1
	50				1	5	4
Vinyon	5				9	1	
	10			1	7	1	1
	30						10
	50						10

38. It can be seen from the data in Table IX that at the three lower exposure times there is no significant difference among the coated, impregnated, and rayon types. The 30 minute Vinyon Cloth caused 100% vesication and is therefore significantly less effective than the other cloths in retention of vesicants. The tests therefore gave no indications of improvement over the coated type by the use of other methods of incorporation of the carbon.

(3) Destruction of Absorbed Vesicants with Chloroamides

39. There are two possible means of destroying vesicants on the carbon cloths by the use of chloroamides: (1) incorporation of the chloroamide in the carbon cloth such that it accelerates the decomposition of the vesicant as the carbon absorbs it, and (2) dusting or coating of previously contaminated carbon cloths to remove or destroy the vesicant stored on the carbon.

40. Under the first method, attempts were made to incorporate chloroamide only into the carbon cloth, leaving out the other chemicals used for chloroamide impregnations. Carbon cloths representing the four different types were immersed in a concentrated solution of S-330 base hydrochloride and chlorinated

while still wet. The resulting cloths, in addition to the activated carbon, then contained, on the average, 0.1 mg. Cl^+/cm^2. Resulting chemical break times were comparable to the break times of the carbon cloth alone, both before and after accelerated storage tests. However, due to the inability to wash all the acid from the cloths after chlorination, the cloths tendered to nearly zero tensile strength after a few days storage at room temperature. Because of this phenomenon, physiological tests for determination of vesicant desorption rate were postponed.

41. The second method attempted was exposure of a previously contaminated cloth to the chemical action of chloroamides. Samples of (1) the NDRC August Model (later model of coated cloth similar to the NDRC March Model; (2) NDRC July Model, impregnated; (3) Costa Model, rayon; and (4) Vinyon were exposed to 3800 CT H vapor (see Table XVI for actual H content). A portion of each cloth was thoroughly dusted with micronized CC-2 and allowed to stand at room conditions for 16 hours. After this period, the CC-2 powder was thoroughly brushed off the surface of the cloths. The eight different samples (four cloths, treated and untreated) were then cut into squares and tested as previously described in direct contact with the skin, covered with adhesive tape. The patches were worn for 4 hours by 5 men in each group. Room conditions were approximately 75°F and 45% relative humidity. Readings were taken at 48 hours. The men wore comparable treated and untreated samples on opposite arms to obtain a more direct comparison between the effect of the treated and untreated cloth on each man. The results are given in Table X.

Table X

Effect on Vesicant Retention by Dusting with Chloroamide

Untreated Cloths

Cloth Type	Results (48 hours) 0	E-?	E-	E	E+	V
NDRC July Model		2	1	2		
NDRC March Model	1	2	1	1		
Rayon	1	3	1			
Vinyon		3	2			

Treated Cloths

Cloth Type	0	E-?	E-	E	E+	V
NDRC July Model		1	3	1		
NDRC March Model			5			
Rayon	2	2	1			
Vinyon		1	3	1		

42. It is evident from the results of this test that dusting the contaminated cloths with micronized CC-2 had little or no effect on the desorption of the stored vesicant.

III. Evaluation of Laundering Agents

43. From previous studies, both by NRL and NDRC, common soaps and many other detergents were found to poison the activated carbon in carbon cloths. Subsequent searches by NDRC investigators for a satisfactory detergent for carbon cloths led to the use of Kalye-25 as a cleansing agent. However, after some use, this detergent was also found to have an adverse effect on the carbon activation in that the protective capacities of the cloths were lowered significantly. Kalye-A, a modification of Kalye-25, and Triton-770 were then suggested as being more desirable for the laundering of carbon cloths. Tests were made using these two agents, Nacconol NR (detergent used for chloroamide impregnated clothing) and water with no detergent added. Launderings were carried out in a standard home laundry machine using 0.2% (by weight) of detergent in 15 gallons of water at 60°C. Each wash consisted of 15-minutes washing in the detergent solution followed by three separate 5-minute rinses in fresh water. Three yards each of NDRC August Model (coated), NDRC July Model (impregnated), Costa Model (rayon), and Vinyon were included in each wash. A series of 10 launderings was made using each agent, with analyses for carbon content and chemical break times against H vapor being run on alternate launderings. The results of the carbon analyses, the H penetration times, and the calculated unit protective capacities of the cloths may be found in Table XI.

44. The amount of carbon in each cloth was determined by the method described in NRL Memorandum to the Director "Determination of Charcoal on Charcoal-Impregnated Cloth," dated October 16, 1942; i.e. digestion of a sample in super-concentrated HCl followed by filtration and weighing of the residual carbon. The Vinyon Cloth was not analyzed since the method of analysis is not applicable to this type of fabric.

Table XI

Effect of Detergents on the Protective Capacity Of Carbon Cloths

A. Laundering Agent--Water

Cloth Type	Wash No.	Mg. C/cm.^{2}	Time of H Penetration (min.)	Min. H. Protection by 1 mg. C/cm.^{2}
NDRC August Model (coated)	0	3.73	270	73
	1	3.71	248	67
	3	2.90	262	90
	5	2.16	325	150
	10	2.38	343	144
NDRC July Model (impregnated)	0	4.42	330	75
	1	2.06	197	96
	3	1.76	235	139
	5	1.23	110	90
	10	1.06	136	128
Rayon	0	5.57	701	126
	1	6.66	>975	>145
	3	6.41	>982	>153
	5	7.51	>1091	>145
	10	5.83	760	130
Vinyon	0		414	
	1		319	
	3		319	
	5		385	
	10		542	

B. Laundering Agent--0.2% Kalye A

NDRC August Model (coated)	0	3.73	270	73
	1	3.96	387	97
	3	2.62	348	133
	5	2.59	287	111
	10	1.95	174	89
NDRC July Model (impregnated)	0	4.42	330	75
	1	2.33	160	69
	3	1.40	118	84
	5	1.23	104	84
	10	1.00	85	85

Table XI continued---

B. Laundering Agent--0.2% Kalye A

Cloth Type	Wash No.	Mg. C/cm.^{2}	Time of H Penetration (min.)	Min. H. Protection by 1 mg. C/cm.^{2}
Rayon	0	5.57	701	126
	1	7.38	629	86
	3	7.99	708	89
	5	8.26	1072	130
	10	9.18	780	85
Vinyon	0		414	
	1		708	
	3		544	
	5		518	
	10		576	

C. Laundering Agent--0.2% Triton 770

NDRC August Model (coated)	0	3.73	270	73
	1	3.78	330	87
	3	3.31	269	81
	5	3.23	144	45
	10	2.40	54	22
NDRC July Model (impregnated)	0	4.42	330	75
	1	1.87	218	117
	3	1.49	86	58
	5	1.59	44	28
	10	1.20	30	25
Rayon	0	5.57	701	126
	1	5.99	606	101
	3	6.80	394	58
	5	7.68	476	62
	10	10.29	605	59
Vinyon	0		414	
	1		275	
	3		236	
	5		160	
	10		88	

D. Laundering Agent--0.2% Nacconol NR

NDRC August Model (coated)	0	3.73	270	73
	1	3.16	240	76
	3	3.56	161	45
	5	3.45	121	35

Table XI continued----

D. Laundering Agent--0.2% Nacconol NR

Cloth Type	Wash No.	Mg. C/cm.^{2}	Time of H Penetration (min.)	Min. H. Protection by 1 mg. C/cm.^{2}
NDRC July Model (impregnated)	0	4.42	330	75
	1	2.30	101	44
	3	1.88	52	28
	5	1.61	32	20
Rayon	0	5.57	701	126
	1	5.45	223	41
	3	5.90	78	13
	5	7.27	106	15
Vinyon	0		414	
	1		345	
	3		81	
	5		40	

45. From the data presented in Table XI, it is evident that water alone or a 0.2% solution of Kalye-A had no adverse effects on the protective capacity of the activated carbon, whereas the solutions of Triton 770 and Nacconol NR gradually poisoned the carbon. Although the carbon content of the NDRC August and July Models was steadily decreased by laundering, the activation of the remaining carbon stayed at a high level when water alone or Kalye-A was used in the laundering process. The unusual, but rather constant, increase in apparent carbon content of the Rayon cloth may be attributed partially to shrinkage of the cotton fiber used in the weave of this 2-ply cloth.

46. It should be pointed out that poisoning of the carbon as indicated by the lower protective capacity value may have no meaning from the physiological standpoint since it does not give a measure of the desorption factor.

IV. Reactivation of Poisoned Carbon Cloths

47. It has been previously discovered that it is possible to reactivate carbon cloths that have been partially or wholly poisoned by vesicants and other contaminants. A Memorandum to the Director, C-S77-2, dated March 8, 1943 listed data showing that, in certain instances of poisoning, the reactivation could be accomplished with hot water or hot detergent solutions, while dry cleaning would bring about a reactivation in almost all cases. Reactivation of cloths poisoned by perspiration, smokes, soap, organic vapors, and vesicants has

been previously reported. The following data deals almost entirely with the reactivation of samples of cloth or suits which have been poisoned or contaminated by wearing and/or exposure to H vapors in a gas chamber. Tables XII and XIII show the results of H analyses and chemical break times, respectively, of suits worn in a gas chamber. The suits were made of NDRC August Model cloth (carbon-coated herringbone twill). Samples for the various analyses were cut from the suits at intervals during the tests.

48. Laboratory launderings were carried out as previously described in the section on laundering. Plant launderings were carried out in a Navy portable plant as follows: one 15-minute wash with 0.2% Kalye-A at 60°C and four 3-minute rinses at 35°C. Dry cleanings consisted of a 15-minute rinse with trichloroethylene at 25°C. followed by drying in a tumbler dryer. The method of analysis for H gives a measure of total sulfides, so that thiodiglycol is included in the result as well as H.

Table XII

Removal of H from Contaminated Suits by Laundering and Dry Cleaning

A. H Content of Suits After Exposure in Gas Chamber

Cumulative CT of H	Cumulative Wear (hrs.)	Suit No.	Area of Suit		Mg. H/cm.^{2}
6000	280	20	Elbow		0.059
			Seat		0.070
			Knee		0.055
				Ave. =	0.061
4800	160	24	Armpit		0.040
			Elbow		0.033
			Seat		0.034
			Knee		0.073
				Ave. =	0.045
4800	99	36	Pocket		0.039
		37	"		0.045
		38	"		0.056
				Ave. =	0.047

Table XII continued----

B. H Content of Swatches Laundered with Kalye A in the Laboratory

Cumulative CT of H	Cumulative Wear (hrs.)	Suit No.	Area of Suit		Mg. H/cm.^{2}
		20	Armpit		0.011
			Elbow		0.033
			Seat		0.015
			Knee		0.013
				Ave. =	0.018
		24	Armpit		0.011
			Elbow		0.018
			Seat		0.006
			Knee		0.010
				Ave. =	0.011

C. H Content of Suits Laundered with Kalye A in a Portable Plant*

19	Pocket	0.006
22	"	0.004
25	"	0.003
27	"	0.005
36	"	0.003
37	"	0.003
38	"	0.003

D. H Content of Suits Dry Cleaned with Triclene in the Laboratory

19	Pocket	0.039
21	"	0.008
22	"	0.031
25	"	0.040
26	"	0.006
27	"	0.034

*Suits dried in tumbler dryer for 75 minutes at a relatively high but unmeasured temperature, due to a faulty temperature indicator.

49. The data in Table XII indicate that a substantial amount of the H was removed by the three different methods used. However, the suits that were laundered did not regain any protective value, while the dry cleaned ones were somewhat impaired. The physiological data are reported in NRL Report P-2239 previously cited. The rather complete removal of H by plant laundering may have resulted from the accidental extreme drying conditions noted in Table XII.

Table XIII

H Penetration Data

Treatment of Suit	Area of Suit		H Break time (min.)
(a) None	Any		270 (ave.)
(b) Exposed to CT 4800 of H and worn 160 hours	Armpit		142
	Elbow		91
	Seat		88
	Knee		130
		Ave. =	113
(c) Samples from (b) lab-laundered in Kalyé A	Armpit		167
	Elbow		110
	Seat		140
		Ave. =	139
(d) Samples from (c)(after penetration tests) dry cleaned CCl_4	Armpit		239
	Elbow		134
	Seat		167
		Ave. =	180
(e) Sample from (b) laundered in Kalye A	Knee		149
(f) Samples from (b) Dry Cleaned in Triclene	Pocket		179
	"		283
	"		278
	"		167
		Ave. =	227

50. The data in Table XIII shows that the exposed and worn suits partially regained their H capacity by both laundering and dry cleaning. Dry cleaning appeared to reactivate the carbon to a slightly greater extent than laundering. Further physiological tests made with the reactivated suits (NRL Report P-2239) showed that no protective value was restored by laundering whereas a partial restoration was brought about by dry cleaning.

51. Further data on the reactivation of poisoned carbon cloth by dry cleaning methods was obtained on samples from suits used in two wearing trials conducted at Bainbridge Naval Training Station. Details of these wearing trials are given in Section V of this report. The data on dry cleaning of these poisoned samples are given in Tables XIV and XV.

Table XIV

Perclene Reactivation of Suits Worn in First Bainbridge Trial

Position of Sample	H Break Times After Wearing	H Break Times After Dry Cleaning
A. Original (NDRC March Model)	411	-
B. Suits worn one week; laundered once in Kalye 25		
Armpit	191	197
Back	120	215
Crotch	111	216
C. Suits worn two weeks; laundered once in Kalye 25		
Armpit	28	134
Back	55	186
Crotch	88	154
D. Suits worn three weeks; laundered twice in Kalye 25		
Armpit	17	144
Back	60	110
Crotch	78	226

Table XV

Triclene Reactivation of Suits Worn in Second Bainbridge Trial

Sample	After 6 weeks Wear: H Break Time (min.)	After 6 weeks Wear: Min. Protection by 1 mg. C/cm.^{2}	After Dry Cleaning: H Break Time (min.)	After Dry Cleaning: Min. Protection by 1 mg. C/cm.^{2}
Original (NDRC August Model)	270	73		
47B-9 Armpit	44	70	-	-
Shoulder	44	36	40	32
Seat	20	14	56	35
Knee	82	44	131	71
Pocket	82	45	128	71
47B-10 Armpit	41	29	-	-
Shoulder	122	62	149	75
Seat	48	23	113	53
Knee	252	97	130	50
Pocket	101	43	150	63

52. A comparison of the amount of reactivation obtained by laundering and dry cleaning methods was made using the four different types of carbon cloth previously mentioned (NDRC August Model, NDRC July Model, Rayon, and Vinyon). The four samples of cloth were exposed in a gas chamber to 3800 CT of H vapor. The H pick-up and chemical break times before and after exposure are given in Table XVI.

Table XVI

H Content and Penetration Time after Exposure to 3800 CT of H Vapor

Sample	H Break Times (Min.) Original	After Exposure	Mg. H/cm.^{2}
NDRC August Model	270	260	0.243
NDRC July Model	330	167	0.235
Rayon	701	>447	0.095
Vinyon	414	415	0.112

53. Portions of the contaminated cloths were subjected to one laundering in Kalye A and to one dry cleaning in Triclene. After the laundering and dry cleaning, H analyses and break times were determined and the results are given in Table XVII.

54. The H penetration times for the NDRC July Model and Vinyon fabrics appear to have dropped considerably when dry cleaned. This is presumably due to the solvent action of triclene on the Vinyon fiber and on the binder used in the July Model impregnation.

Table XVII

H Content and Penetration Time after Decontamination

Sample	H Break Time (Min.)	Mg. H/cm.^{2}
A. Laundered Samples		
NDRC August Model	413	0.018
NDRC July Model	179	0.016
Rayon	>544	0.014
Vinyon	437	0.025
B. Dry Cleaned Samples		
NDRC August Model	555	0.018
NDRC July Model	139	0.011
Rayon	655	0.032
Vinyon	45	0.009

V. Wearing Trials of Suits Prepared from Carbon Fabrics

55. Two separate wearing trials of suits prepared from carbon cloth were carried out at the Bainbridge Naval Training Station. The first trial was conducted in July 1943 with six suits prepared from the NDRC March Model cloth (Herringbone Twill coated with a carbon-viscose rayon mix). The suits were worn 8 hours per day, 5 days per week by recruits in the normal training course. The average temperature throughout the 3-week test was 76°F and the relative humidity 60%. At least once each day, the recruits were thoroughly perspiring. At the end of each week's wear, the suits were laundered in 0.2% Kalye-25 at 60°C for 15 minutes, followed by three 5-minute rinses. Two suits were withdrawn each week and tested for loss of H capacity. The results are shown in Table XVIII.

Table XVIII

Protective Capacity of Suits from First Wearing Trial

Sample	H Break Time (Min.)			
	Armpit	Back	Crotch	Average
Original	480	188	366	376
1 Week Wear, 1 Wash	147	120	258	186
2 Weeks Wear, 1 Wash	28	55	88	57
3 Weeks Wear, 2 Washes	17	60	78	54

56. The data in Table XVIII show the suits to have been poisoned to a considerable extent during this wearing trial. The loss of protective capacity to some extent was due to a mechanical loss of carbon during wear and laundering. This statement is substantiated by the fact that the men's undergarments were considerably blackened by the carbon from the suits. Also, the wash water from the launderings was blackened by the carbon removed from the suits. To determine the extent of H capacity loss which can be attributed to poisoning, rather than loss of carbon, the samples were extracted with perchloroethylene. The H capacity of the extracted samples is given in Table XIX.

Table XIX

H Protective Capacity of Dry Cleaned Samples

Sample	H Break Time (Min.)			
	Armpit	Back	Crotch	Average
1 Week	215	216	197	209
2 Weeks	186	154	134	158
3 Weeks	110	226	144	160

57. From the results of the dryeleaning, as listed in Table XIX, it appears that the loss of protective capacity by the worn suits was due, to a great extent, to poisoning of the activated carbon.

58. The second wearing trial was conducted in September, October, and November 1943, with 10 suits prepared from the NDRC August Model cloth (same type as the March Model). The suits were worn 8 hours per day, 5 days per week for a period of six successive weeks under conditions varying from mild to the most strenuous abuse of the suits. At the end of each week, the suits were laundered in 0.2% Kalye-25 at 90°F for 15 minutes, followed by three 5-minute rinses.

59. At the start of the test, there were several cases of skin irritation in the region of the knees due probably to the stiffness of the cloth when new. All irritation ceased after a few days wear had softened up the cloth. Throughout the test, there was a continued crocking of the carbon coating such that the men's undergarments were considerably blackened. This effect gradually decreased throughout the wearing trial. The water used in laundering was also blackened each time by the carbon lost from the suits. At the conclusion of the wearing trial, two suits were analyzed for total H capacity and for carbon content. The results are given in Table XX.

Table XX

Protective Capacity of Suits from Second Wearing Trial

Sample	H Break Time (Min.)	Mg. C/cm.^{2}	Min. H Protection by 1 mg. C/cm.^{2}
NDRC August Model cloth (original)	270	3.73	73
Suit No. 47B-9			
Armpit	44	0.63	70
Shoulder	44	1.24	36
Seat	20	1.58	13
Knee	82	1.86	44
Pocket	82	1.81	45
Suit No. 47B-10			
Armpit	41	1.43	29
Shoulder	122	1.98	62
Seat	48	2.12	23
Knee	252	2.59	97
Pocket	101	2.36	43

60. From the data in Table XX, it can be seen that, in the majority of instances, the samples taken from the worn suits were partially poisoned. It can also be seen that 30 to 75 percent of the carbon coating was removed during the wearing trial.

61. The samples used to obtain the data for Table XX were dry cleaned for 15 minutes in CCl_4 and H capacity tests redetermined to determine the degree of reactivation that could be obtained. Table XXI gives a summary of the H capacities after dry cleaning.

Table XXI

Protective Capacity after Dry Cleaning

Sample	H Break Time (min.)	Mg. C/cm.^{2}	Min. H Protection by 1 mg. C/cm.^{2}
Suit No 47B-9			
Armpit	-	-	-
Shoulder	40	1.24	32
Seat	56	1.58	35
Knee	131	1.86	71
Pocket	128	1.81	71
Suit No. 47B-10			
Armpit	-	-	-
Shoulder	149	1.98	75
Seat	113	2.12	53
Knee	130	2.59	50
Pocket	149	2.36	63

62. The comparative capacity values shown in Tables XX and XXI show that there was a slight degree of reactivation obtained by dry cleaning the samples in CCl_4.

63. The remaining 8 suits from the second Bainbridge wearing trial were used for a series of gas chamber tests. The suits were exposed in a gas chamber to varying amounts of H vapor and worn continuously until adverse physiological effects were obtained. This study, in addition to data on the chamber trials of new suits made from NDRC August Model cloth, is described in NRL Report P-2239, "Chamber Tests with Human Subjects. IV. Tests of Carbon Clothing Against H Vapor."

64. In order to determine the relative physiological protective efficiencies of four types of carbon cloth, a series of arm chamber tests were run. A 3-inch band of each type of cloth was exposed to H vapor. The area covered by the band of cloth was the forearm, midway between wrist and elbow.

A detailed description of the method used is contained in NRL Report No. P-2219, entitled "Chamber Tests with Human Subjects. III. Design, Operation and Calibration of a Chamber for Exposing Forearms to H Vapor." Each wearing consisted of exposure to 1200 CT of H vapor. Twenty-four hours after each exposure, the physiological reaction was noted and, if not adverse, another exposure was made. The procedure was continued until a reaction of E or higher was obtained, at which time that particular sample was removed from the test. The physiological readings throughout the tests are listed in Table XXII.

65. It may be seen from the data in Table XXII that the Costa type Rayon cloth provided protection for a considerably longer time than did any of the other types. The impregnated cloth and the vinyon fabric gave the poorest protection. The coated type cloth, which has been most thoroughly investigated in the form of actual protective suits, had an intermediate protective value.

Table XXII

Physiological Results of Arm Chamber Tests of Different Type Carbon Cloths

Type	24 Hour Readings After Exposure Number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	18
ated	0	E-	E-	E-	E-	E-	E-	(E)	E/					
	0	E-?	E-?	E-	E-	E-	E-	(E)	E/					
yon	0	E-	E-	E-	E-	E-	E-	E-?	E-	E°	E°	E°	E°	--- E°
	0	0	E-	E-	E-	E-?	E-?	E-?	E-	E°	E°	E°	(E+)*	
-	E-	E-	E-	E°	(E)	E+/	.							
gnated	0	0	E-	E-	E°	(E+)	(NPV)							
ıyon	0	E-	E-	E°	(E)	NPV/								
	E-	E-?	E-	E°	E°	(E+)	E+/							

() denote a break (subject removed from test)
/ denote 48 hour readings after last exposure
* This reaction was caused by a leak at the edge of sleeve and not by a penetration of the cloth.

SUMMARY AND CONCLUSIONS

Part I. Storage and Weathering

1. An investigation was made of the behavior of three different types of carbon cloth. These types included a coated fabric, an impregnated fabric, and a fabric woven with cotton and rayon threads in which the rayon fibres contained carbon. Outdoor exposure of such cloths up to six months showed that the protective capacity was not seriously reduced for the coated or rayon types. The impregnated type retained only 25% of its initial capacity after five months exposure. This was attributed principally to deterioration of the binding agent with a consequent mechanical loss of carbon.

2. Storage of carbon cloths at room temperature in intimate contact with chloroamide cloths showed that the chloroamide cloths have little, if any, poisoning effect on activity of the carbon.

Part II. Vesicant Desorption.

3. The vesicant effects of carbon cloths contaminated with H were investigated over a range of contamination levels and different conditions of wear. The tests were carried out by the application of contaminated patches to the forearms of men. It was found that the degree of vesication increased not only with the contamination level but also with the time of wear of contaminated cloth.

4. Attempts were made to obtain a laboratory test by which the desorption of H from contaminated cloths could be ascertained, measured, and correlated with the physiological effects. Use of the Spotted Dick test throughout a range of temperatures from 25°C-70°C and relative humidities from 0 to 100% gave erratic and inconclusive results. The use of DB-3 test papers and DB-3 tubes likewise gave uhreliable tests. No test was found which could be correlated with physiological results.

5. An investigation was made of various means of preventing or minimizing the desorption of H from contaminated cloths. Cloths impregnated with different type carbons - different base carbons as well as chemically impregnated carbons - were contaminated to different levels and tested physiologically by the patch test method. None of the special carbons tested showed any marked improvement over the N-44 carbon previously used. An aging period of 3 days after contamination likewise did not decrease the desorption of vesicant from the contaminated samples.

6. Physiological tests were made to determine whether the manner of incorporation of the carbon had any effect on the H desorption. The four types - coated, impregnated, rayon, and vinyon - were tested. While vinyon cloth proved to be even less effective than the other types, none showed any improvement in these tests.

7. Physiological patch tests with contaminated cloths which had been allowed to stand thoroughly dusted with chloroamide for 16 hours did not show any significant destruction of vesicant in comparison with untreated cloths.

8. Incorporation of a chloroamide directly into a carbon cloth was investigated. Vapor phase chlorination of S-330 on carbon cloths gave samples with a high vesicant capacity, but the cloth deteriorated from acid which could not be thoroughly washed out after the impregnation.

Part III. Evaluation of Laundering Agents

9. Four types of carbon cloth were laundered in each of the following systems: plain water, 0.2% solution of Kalye A, 0.2% solution of Triton 770, and 0.2% solution of Nacconol NR. A series of 10 successive launderings showed that water and Kalye-A had little effect on the protective capacity of the carbon, while Triton 770 gradually poisoned the carbon and Nacconol NR rapidly poisoned the carbon. In all cases carbon was removed from the coated and impregnated cloths by the launderings, with the impregnated cloth showing the greater loss of carbon. No carbon was lost from the rayon type cloth.

Part IV. Reactivation of Poisoned Carbon Cloths

10. Plant and laboratory launderings with Kalye A and dry cleanings with carbon tetrachloride and Triclene were carried out on garments and cloth samples which had been previously contaminated with H. In all cases, there was a removal of H from the cloth, as evidenced by H analyses. It was possible to remove a higher percent of the H by dry cleaning than by laundering. However, the impregnated and vinyon type cloths deteriorated on dry cleaning due to the solvent action of the dry cleaning agent on the binder and the vinyon fibres.

Part V. Wearing Trials

11. Two separate wearing trials of suits made from the coated type cloth were carried out at the Bainbridge Naval Training Station. The suits were subjected to a range of treatment varying from mild to rough conditions during summer and fall weather.

12. Crocking of the carbon coating onto the mens' underclothing was severe especially at the start of the tests. Carbon was also removed during each laundering. At the end of the 6-week trial, approximately 40-60% of the carbon remained on the suits.

13. The total H capacity of the suits decreased throughout the trials because of removal of carbon and partial poisoning of the remaining carbon. However, these garments were found to give protection equivalent to new unworn garments when subjected to chamber tests.

14. Four different types of carbon cloths were tested in an arm chamber to determine the amount of protection against H vapor relative to the type of cloth. The coated fabric, the impregnated fabric, and the vinyon fiber fabric exhibited roughly equivalent protective value. However, the fabric woven with rayon fibers containing carbon was extraordinary in its behavior and showed an unusually high degree of protection.

RECOMMENDATIONS

1. The investigation and development of activated carbon as an anti-vesicant agent for protective clothing should be continued. Particular emphasis should be placed on efforts to eliminate or minimize the desorption of vesicant agents from contaminated clothing.

2. Indications of the unusual protective value shown by the type of fabric woven with rayon fibres containing activated carbon should be more fully investigated.

3. At the present stage of development protective clothing containing activated carbon as an anti-vesicant agent cannot be recommended for service use.