DECOMPOSITION OF AND PRESSURE DEVELOPED BY MUSTARD GAS IN STEEL SHELL AT 60° C.¹

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It has been determined qualitatively that crude mustard gas (dichloroethyl sulfide) slowly attacks iron, and that it is itself slowly decomposed at room temperatures by contact with iron. Since hydrochloric acid is one of the products of this decomposition of mustard gas, and since mustard gas as commercially produced is never quite dry, the effect of the decomposition is essentially a corrosion of the iron by the hydrochloric acid with liberation of hydrogen. Since the plant of Edgewood Arsenal was loading steel shell with crude mustard gas for shipment overseas, it became highly desirable to ascertain:

(1) The extent of decomposition of the mustard gas in the steel shells during a two weeks' journey in cargo vessels, at temperatures as high as 50° C.

(2) The maximum pressure that would obtain inside of the shell, in order to make provisions for a sufficiently tight or leak-proof booster-shelljoint, and to provide boosters with sufficient wallthickness to prevent caving in.

Steel shell filled with mustard gas were therefore kept at 60° C. for a period of 2 wks., in order to determine the rate of decomposition and to measure the pressures developed.

The mustard gas shipped was prepared by two processes, both based upon the interaction of sulfur monochloride and ethylene. The one (the original process, designated in this paper as Process A) employed no initial charge of mustard gas as catalyzer, was operated at 60° C., and employed lead-lined reactors; the other (the Levinstein process, designated as Process B) maintained a 70 to 75 weight per cent concentration of mustard gas throughout the run until all the sulfur monochloride had been added, was operated at 30° to 35° C., and employed simple iron reactors. The products differed considerably in color, purity, amount of sulfur held in colloidal solution, acidity, etc. Both kinds of crude mustard were investigated. The vast majority of the gas, however, was prepared according to Process B.

METHODS OF INVESTIGATION

In order to gain information on the two points stated in the beginning of this paper, two series of experiments were made. The methods may be outlined as follows:

SERIES 1—Three hundred cc. samples of analyzed crude Process A and Process B mustard gas were placed in several 75 mm. shell. The shell were tightly closed by means of rubber stoppers and were kept in a thermostat at 60° C. ($\pm 1^\circ$) for a period of 16 days for the Process B samples, and 8 days for the Process A samples. A test sample was taken every two days in the order of shell number, two successive samples being taken from each shell. Two shell contained crude Process A and four shell Process B mustard gas, both of excellent quality initially. To detect any abnormal behavior during the testing period, a final sample was taken from each of the

first four shell at the end of 16 days for the determination of acidity and final melting point.

SERIES 2—Three hundred cc. samples of analyzed crude Process B mustard gas were placed in 75 mm. shell connected with mercury manometers. Also, samples of Process B mustard gas which had been treated with gaseous ammonia (this procedure precipitating out about 7 to 8 per cent of the colloidal sulfur and destroying the HCl per cent) and of Process A mustard gas in which gas oil had been substituted for colloidal sulfur (by the process of extraction) were also placed in shell similarly arranged. As a check, samples of each material were placed in glass containers, producing the same void as in the steel shell, and connected to mercury manometers.

TABLE I—PROGRESSIVE DECOMPOSITION OF MUSTARD GAS IN STEEL SHELL

SAMPLE	Shell No.	Days in Shell	Melting Point (Crude) °C.	Melting Point Lowering (Crude) °C.	Relative Purity of Mustard Gas, Per cent	Drop in Percentage Purity	Per cent Acidity as HCl	Increase in Acidity
Process B	1	0	8.00	—	81.8	—	0.160	—
	2	2	7.90	—0.10	81.5	0.3	0.180	0.020
	1	4	7.50	—0.50	80.3	1.5	0.382	0.222
	2	6	7.20	—0.80	79.4	2.4	0.417	0.257
	2	8	7.05	—0.95	79.0	2.8	0.639	0.479
	3	10	7.10	—0.90	79.1	2.7	0.910	0.750
	3	12	6.95	—1.05	78.7	3.1	0.645	0.485
	4	14	6.10	—1.90	76.1	5.7	1.387	1.227
Process A	4	16	6.00	—2.00	75.7	6.1	1.535	1.375
	5	0	10.30	—	88.9	—	0.270	—
	5	2	9.40	—0.90	85.1	2.8	1.028	0.758
	4	4	9.20	—1.10	83.5	3.4	1.308	1.038
	6	6	9.60	—0.70	86.8	2.1	0.968	0.698
	6	8	9.40	—0.90	86.1	2.8	1.009	0.739

Zero readings were taken on each manometer at 30° C., the temperature of the bath when the manometers were sealed on. All connections had been tested for leaks. The temperature of the thermostat was raised to 60° C. and maintained at this temperature ($\pm 1^\circ$ C.) for over 10 days. An initial pressure reading was made one hour after the thermostat had been adjusted to 60° C. Subsequent manometer readings were made twice daily (at 8:30 A.M. and 4:30 P.M.).

FIG. 1—RELATIVE PURITY AND ACIDITY AS A FUNCTION OF TIME

METHODS OF ANALYSIS

The tests for the determination of the progressive decomposition consisted of vacuum distillations, melting-point determinations on the crude and the distilled

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samples, and acidity determinations. The percentage purity of the distilled product and the relative percentage purity of the crude were gaged by an empirically determined purity-melting point relation.¹ Acidity determinations were made by adding chloroform (to dissolve the mustard gas) and water, and titrating with a standardized sodium hydroxide solution.

In Series 2, melting-point, acidity, and purity tests were made only at the beginning and at the end of the 10-day period.

TABULATION OF RESULTS

The results obtained in Series 1 are presented in Tables I and II; in Fig. 1 are presented the melting-point lowerings and acidity increases as related to time in days, and in Fig. 2 the relation of melting-

FIG. 2—MELTING-POINT LOWERING AS A FUNCTION OF ACIDITY INCREASE

point lowering to acidity increase. The results of the analysis of initial and final materials of the shell of Series 2 are presented in Table III. Net decomposition pressures were obtained by subtracting initial readings at 60° C. from final readings at 60° C. The thermostat temperature was lowered to 30° C. at the end of the test period, and pressures were again read. Fig. 3 gives the total pressures corrected to initial barometer and initial zero readings on manometers. Fig. 4 gives the same relation of pressure with respect to time with the additional correction for thermal expansion from 30° C. to 60° C. The lowering of pressure due solely to gas absorption on cooling to 30° C. is shown in Fig. 3 by the dotted lines at the end of each curve.

TABLE II—MELTING POINTS AND ACIDITY OF MUSTARD GAS AT END OF 16-DAY PERIOD

SAMPLE	Shell No	Melting Point °C.	Total M.-P. Lowering °C.	Acidity	Total Increase in Acidity
Process B	1	8.0	...	0.160	...
	2	4.5	3.5	2.330	2.770
	3	5.0	3.0	1.907	1.747
	4	5.8	2.2	0.885	0.725
	5	6.0	2.0	1.335	1.375
Process A	5	10.3	...	0.270	...
	6	7.7	2.6	4.690	4.420
	6	8.9	1.4	1.862	1.592

Table II presents the results of determinations of the melting point and the acidity on the residual mustard gas in the shell of Series 1 at the end of 16 days.

¹ Bureau of Mines, *Organic Report* 28, April 6, 1918.

TABLE III—ANALYSIS OF ORIGINAL AND FINAL MUSTARD GAS IN PRESSURE DEVELOPMENT TESTS (AT END OF 10 DAYS)

SAMPLE	Melting Point °C.	Melting-Point Change	Relative Purity Per cent	Change in Purity	Percent Acidity, as HCl	Increase in Acidity
Original Crude Process B	8.0	...	82.4	...	0.175	...
Process B from steel shell	6.4	-1.6	76.5	-5.9	2.040	1.865
Process B from glass container	7.6	-0.4	81.2	-1.2	0.456	0.281
Process B, ammonia-treated	8.1	...	82.7	...	0.005	...
Ammonia-treated, from shell	8.1	±0.0	82.7	±0.0	0.422	0.417
Ammonia-treated, from glass container	8.6	+0.5	84.4	+1.7	0.012	0.007
Original Sample Process A + 12 per cent oil	7.9	...	82.1	...	0.073	...
Process A + 12 per cent oil, from shell	7.2	-0.7	80.0	-2.1	0.661	0.588

DISCUSSION OF RESULTS

The data obtained in Series 1 offer substantial proof of a progressive decomposition of mustard gas in steel shell at temperatures near 60° C. This time-relative purity relation for Process B mustard gas is practically a linear function (see Fig. 1). The increase of acidity with time in the closed steel shell is also presented in the figure, showing practically a uniform rise. An increase in acidity goes hand in hand with a lowering of melting point and a decrease in actual mustard gas content. This is shown in Fig. 2.

FIG. 3—DECOMPOSITION PRESSURE OF MUSTARD GAS AT 60° C. (Not Corrected for Thermal Change)

The Process A mustard gas tests were continued over a period of only 8 days, and though the results are not as concordant as those on Process B mustard gas, the decomposition and the increase in acidity proceed in the same general way as for Process B.

FIG. 4—DECOMPOSITION PRESSURE OF MUSTARD GAS AT 60° C.
(Corrected for Thermal Change)

Analysis by means of vacuum distillation does not yield satisfactory results, because the amount of sulfur precipitated out of colloidal solution varies with the time, and hence the analysis of the supernatant liquid is not a true criterion of the purity of the sample. Further, an actual decomposition of the mustard gas may be counterbalanced by a precipitation of sulfur, the precipitated sulfur adhering to the sides of the shell. The reliable criterion for determining the extent of decomposition was the melting-point determination on the undistilled mustard; since in this determination the colloidal sulfur does not affect the melting point, while the decomposition products do. Hence, a relative purity based upon these melting points is recorded, and the results given graphically in Fig. 1.

In Series 2, the relation of melting-point lowering and total acidity is again confirmed; while the relation is not the same quantitatively, the general behavior and trend is the same. The deviation may be due to several causes, but it would be idle curiosity to attempt to make an explanation.

By reference to either Figs. 3 or 4, it will be noted that a maximum pressure development is attained in about 9 days with crude Process B mustard gas. With the ammonia-treated mustard gas a negative pressure actually obtained for 3 days, after which a slight positive pressure was built up. The negative pressure is very likely the result of the neutralization of the ammonia in solution and as a gas by the hydrochloric acid formed by hydrolysis. It is possible that

if the tests had extended over a longer period, a pressure as high as with the crude mustard gas would have been obtained. The pressure developed by the ammonia-treated mustard gas in glass is practically nil, and the acidity developed is very slight.

The gas oil-mustard gas mixture in general shows a behavior similar to that of the ammonia-treated materials for the earlier part of the test. However, the pressure soon develops more rapidly and would undoubtedly reach a maximum sooner.

All samples of mustard gas in steel uniformly turned deep black, while the samples in glass remained orange-yellow. (A sample of crude Process B mustard gas, which was a light orange-yellow originally and which was sealed up in a glass tube, turned a deep black after about 16 mo. A sample of pure, colorless mustard gas, however, was still perfectly clear even after 20 mo.)

CONCLUSIONS

1—A decomposition of both Process A (original 60° C. process) and Process B (Levinstein) mustard gas takes place in steel shell at 60° C. The extent of the decomposition is not serious even under the severe conditions of the investigation.

2—Sulfur is deposited in solid form in shell in amounts ranging from 5 to 8 per cent of the liquid content of the shell.

3—The pressure developed in the ordinary steel shell is at most barely two atmospheres in any one shell. This seems to be a maximum or equilibrium pressure, reached after about 9 days.

4—The acid content increases considerably, but the concentration is not sufficiently high to cause serious corrosion.

5—A preliminary treatment of the mustard gas with ammonia gas serves to delay the formation of pressure. This delay is of sufficient length to warrant the preliminary treatment of mustard gas which is to be stored for some length of time in steel shell or containers.

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THE PRECIPITATION OF SULFUR FROM CRUDE MUSTARD GAS BY MEANS OF AMMONIA¹

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Mustard gas (β,β' -dichloroethyl sulfide) was produced at Edgewood Arsenal by two processes based upon the interaction of liquid sulfur monochloride and ethylene gas. The following equation represents, in brief, the most probable reaction:

The equation, as written, does not indicate the formation of the intermediate compound $\text{ClC}_2\text{H}_4\text{S}\cdot\text{Cl}$ or of the disulfide $\text{S}(\text{C}_2\text{H}_4)_2\text{S}$, both of which have been proved to be present in crude mustard gas. An inspection of the equation, however, indicates that one atomic

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