[redacted]

REPORT NO. M-1698

DATE 18 February 1941

SUBJECT

Partial Report

on

Studies of Grid Alloys
for
Submarine Storage Batteries

BY

FR-1698

NAVAL RESEARCH LABORATORY

BELLEVUE, D. C.

U. S. GOVERNMENT PRINTING OFFICE 4--7456

rt No. M-1698
Report on Studies of Grid Alloys for
e Storage Batteries

[redacted]

NRL Report No. M-1698

18 February 1941

[redacted]

NAVY DEPARTMENT

Partial Report
on
Studies of Grid Alloys
for
Submarine Storage Batteries

NAVAL RESEARCH LABORATORY

ANACOSTIA STATION

WASHINGTON, D.C.

Number of Pages:	Text - 7 Tables - 3 Plates - 14
Authorization:	BuEng. let. C-SS/S62(2-15-Ds) of 21 February 1933.
Date of Test:	15 August 1937 to 31 May 1938.
Reported by:	Howard F. Taylor, Contract Metallurgist
Reviewed by:	Parry Borgstrom, Superintendent, Chemistry Division
Approved by:	H. G. Bowen, Rear Admiral, U.S.N., Director
Distribution:	BuShips (5)

ect

[redacted]

TABLE OF CONTENTS

APPENDICES

[redacted]

ABSTRACT

This letter summarizes the results of life-tests on storage batteries of the "starting and lighting" type, using grids made of 14 different alloys. These included compositions of a type which previous work at the Naval Research Laboratory and the National Bureau of Standards had indicated were promising.

The results indicate that grids made of lead containing 2-1/2% antimony, and .05 to .10% silver resist anodic oxidation better than grids of standard composition (8 to 11% antimony) while producing negligible sulfation and self-discharge in the negative plates. The hardness and strength of these alloys is of the same order but somewhat greater than that of the standard composition and is due to the combined effect of the antimony and the silver.

No composition of the series tested containing strontium gave satisfactory positive grids under the conditions of the test although in most instances the outward appearance of the grid proper upon dissembling the cells was excellent. Tests with calcium and barium have, in the past, shown no encouraging results.

[redacted]

AUTHORIZATION

1. This problem was authorized by Bureau of Engineering confidential letter C-SS/S62(2-15-Ds) of 21 February 1933. Other pertinent references are listed as (a) to (h) inclusive.

References:

(a) Preliminary Report on Studies of Grid Alloys for Submarine Storage Batteries of 27 July 1933.
(b) NRL let. SS/19 of 20 April 1934 to Bureau of Engineering.
(c) NRL Report No. M-1052 of 17 May 1934.
(d) NRL Report No. M-1121 of 30 January 1935.
(e) BuEng. let. C-SS/S62(7-31-Y1) of 7 August 1935.
(f) Bureau of Standards Report on Storage Battery Grids Cast from Navy Type Experimental Alloys of 7 December 1936.
(g) NRL let. C-SS/19 of 16 September 1937 to BuEng.
(h) NRL Report No. M-1443 of 6 June 1938.

STATEMENT OF PROBLEM

2. The object of this work was to develop an alloy for storage battery grids, and in particular for the positive grids, which would consist principally of lead and have the durability of lead alloyed with antimony without the undesirable tendency toward contamination of the negative plates with antimony plated on from the positive plates. The principal aim was to find a way of strengthening the metal of the grid to enable it to support its own weight and that of the active paste, and, at the same time, to give it resistance to the attack of nascent oxygen (anodic corrosion). Except perhaps for the "iron-clad" battery anodic corrosion is responsible for the majority of failures of lead batteries of all types. The common and traditional composition of storage battery grids is lead alloyed with antimony, 4-1/2% of this metal conferring maximum resistance to oxygen, but 8 to 11% being necessary to obtain the required strength. The higher percentages are also more readily cast.

FACTS ESTABLISHED BY PAST RESEARCH

3. From the long series of anodic corrosion tests at the Naval Research Laboratory, in conjunction with the two previous life-test series at the Bureau of Standards, several conclusions were drawn. These were set forth in paragraph 5 of reference (h), and the most important are repeated here.

(a) Lead can be very effectively hardened and strengthened by the use of 0.05 to 0.40% of any one of the alkaline earth metals barium, calcium or strontium. Of these three, strontium confers by far

[redacted]

[redacted]

the best resistance to anodic attack, and in conjunction with 0.2 to 2.0% tin gives alloys of high tensile strength and ductility. In the form of solid plates subjected to electrolysis in sulfuric acid some of these alloys suffered much less oxidation than antimony alloys.

(b) However, when cast into actual grids, pasted and made into batteries and given life tests, none of these alloys produced grids which retained their capacity as well as those containing 4% antimony only. The cause of failure was largely loss of active material from the positive plates. This loss of active material was possibly due to the formation of a white layer of surface corrosion product. This may have destroyed the bond between the grid-bars and the active material, but there was at the same time some loss due to breaking up of the grid-bars. In the case of the antimony alloys, failure was due to breaking up of the grid-bars only and there was no sign of white surface corrosion.

(c) It was further discovered that lead, containing 2-1/2% antimony with additional hardening elements (alloy No. VII of par. 2, reference (g)) gave far the most durable positive grids of any of the hardened alloys studied up to that time, and at the same time only an insignificant amount of antimony was plated on to the negatives.

(d) Silver, to the amount of .05% (See alloys 111 & V, table 4 of reference (g)) seemed to improve the character of the positive grids without seriously injuring the negatives.

MATERIALS AND COMPOSITIONS

4. It was decided to make up alloys of 14 compositions based on the results of all previous work. Thirty grids were made of each composition, which was sufficient for four 7-plate cells. In all cases the negative and positive grids in each cell were of the same composition. One set of 4 cells had grids of 4-1/2% antimony. All the rest were 2-1/2% antimony, with varying small percentages of strontium, tin, silver, and tellurium. A full account of the manufacture of these grids will be found in reference (h). The nominal and actual compositions of the alloys are given below in Table 1.

[redacted]

TABLE 1

ALLOY	NOMINAL					ACTUAL				
	% Sb	% Sr	% Sn	% Ag	% Te	% Sb	%Sr	%Sn	%Ag	%Te
A	4.5					4.7				
B	2.5			.05		3.0			.05	
C	2.5			.10		3.4			.12	
D	2.5	.07		.05		2.4	.09		.06	
E	2.5	.07	.20			2.8	.06	.20		
F	2.5	.07		.10		3.9	.04		.10	
G	2.5	.15		.05		2.5	.16		.06	
H	2.5	.15	.20			2.7	.12	.20		
I	2.5	.15		.10		3.2	.13		.11	
J	2.5	.15	.15	.05		2.9	.19	.16	.05	
K	2.5	.15			.02	2.9	.09			*
L	2.5	.15	.20		.02	2.7	.14	.20		*
M	2.5	.15	.40			2.8	.07	.41		
X	2.5	.07	.15	.05		2.4	.06	.16	.03	

* Not reported.

It will be noticed that the tin and silver were recovered in almost the exact percentage added. The antimony is subject to fairly large variations possibly due to segregation since 2-1/2% is slightly above the actual solid solubility limit. The strontium, in spite of careful precautions, also showed wide variations.

[redacted]

STRENGTH AND HARDNESS

5. Hardness was measured by Vickers diamond pyramid with 10 Kg load. Tensile tests were made in a regular tensile testing machine at a rate of loading of 1000 pounds per minute.

TABLE 2

ALLOY	HARDNESS (VP 10)	ULT. TENSILE STRENGTH (psi)	ULT. ELONG. PERCENT
A	13.0	3600	3.1
B	15.5	3650	4.7
C	17.7	5300	4.5
D	17.7	5100	4.5
E	9.5	4550	4.5
F	11.3	*	*
G	16.3	*	*
H	9.3	*	*
I	16.6	*	*
J	18.5	*	*
K	9.8	*	*
L	9.3	*	*
M	11.6	*	*
X	12.8	*	*

* Not determined.

For comparison with the above figures Table X of reference (c) may be examined. It is plain that the alloys of the present series are deficient in both strength and ductility as compared with the former. For example, an alloy of 10% antimony has an ultimate tensile strength of 7670 psi. One of 0.4% strontium and 1.0% tin gave an ultimate tensile strength of 7600 psi and an elongation of 28%.

PREPARATION AND TESTING OF THE CELLS

6. Following is a description by the Bureau of Standards of the preparation and testing of the cells:

7. All grids were pasted with Eagle-Picher battery oxides blended to approximately equal periods of formation for the positive and negative plates. The paste was mixed with sulphuric acid solution and 3/8 per cent lamp black was added to the negative plates. Because of the limited capacity of the mixing machine,

[redacted]

two batches of paste were mixed for the positive plates and two for the negative plates. The first batch in each case was dumped from the machine and when the second batch was ready, the first batch was replaced in the machine and the two batches were then mixed together. This procedure assured practical uniformity of the paste for all plates of the respective kinds.

8. The grids were pasted by hand, the paste being kept covered with wet cloths during the pasting process. The plates were dipped in sulphuric acid as pasted and placed in racks to dry. All plates were allowed to dry in the laboratory for about 1 week.

9. The dry plates were assembled in 7-plate test cells (3 positives and 4 negatives) with moist separators of Port Oxford cedar 5/64 inch thick. Each plate rested upon an individual strip of hard rubber 1/4 inch high which was inserted between the separators at the bottom of the elements to retard the growth of trees at the bottom of the plates.

10. The plates were formed in the battery boxes in series at a charging rate of 3.4 to 3.6 amperes until near the end of the charge when the rate was reduced to 2 amperes. An input of 144 ampere hours was required to form the positive plates and 150 ampere hours to form the negatives. The specific gravity in all cells at the end of the formation charge was within the range 1.110 to 1.120. The average values for the cell voltages and single potentials for the cells of each alloy at the end of the formation charge are given in Table 3.

Table 3

Cell voltage and single potentials at end of formation charge.

(Specific gravity 1.110 to 1.120)

Alloy	Cell	Single potentials	
		Cd pos	Cd neg
A	2.45	2.36	-.09
B	2.46	2.37	-.09
C	2.47	2.36	-.11
D	2.48	2.35	-.13
E	2.50	2.37	-.12
F	2.47	2.37	-.10
G	2.47	2.36	-.11
H	2.48	2.37	-.11
I	2.45	2.36	-.10
J	2.44	2.36	-.18
K	2.49	2.37	-.12
L	2.45	2.36	-.10
M	2.46	2.36	-.10
X	2.46	2.37	-.10

11. After terminating the formation charge, the cells were discharged and the electrolyte was then dumped from the cells and replaced with new electrolyte having a higher specific gravity. After recharging the cells the specific gravity was within the range 1.255 to 1.265 which increased to a practically constant value of 1.270 to 1.280 during the early period of the cycling test.

12. The cycling test consisted of repeated cycles of a discharge for 4 hours followed by a recharge for 8 hours. The discharge rate was 7.5 amperes at the beginning of the test but this was increased somewhat as the capacities of the cells developed and later reduced when the capacities began to decline. The charging rate was adjusted in relation to the discharge rate to provide about 20 per cent overcharge for each cycle. The ampere-hour capacities of the cells were measured, periodically, to an end voltage of 1.75 volts. In order to avoid overdischarging any of the cells during the measured discharges, each cell was disconnected from the circuit as soon as it had reached the end-point voltage.

STEAM-CORROSION TESTS

13. At the time of casting the grids a number of steam-corrosion specimens were prepared and tested at the Naval Research Laboratory. Previous work had shown that there is very good correlation between the results of a steam corrosion test and those of an anodic corrosion test. The specimens were exposed continuously to an atmosphere of air and moist steam at about 212° F. for a period of three months. At the end of this time all specimens were in good condition, ductile and free from intercrystalline oxidation. There was in all cases a decrease of hardness as compared with the original condition but lead alloys in general show changes in hardness with time and these changes are usually in the direction of lower hardness.

CONDITION OF PLATES AFTER DISSEMBLING THE CELLS

14. Great variation was noticed in the condition of the plates as they were removed from the cells, so photographs were made of representative specimens and these are reproduced as A to X of Plates 3 to 14 inclusive. From these pictures Plates B and C were in especially bad condition at the end of the cycling period. Plate D appeared to be in better condition than A but did not last quite as long in the life test. Grids of composition from F to X, inclusive, were not adversely affected by the tests but the paste appears to have fallen out badly from all plates. None of these cells lasted more than 160 cycles, as can be seen from Plate 1, in spite of the fact that even the thin cross bars were intact. This may or may not have been the result of some film forming on the surface of the grid and destroying the bond between it and the plate. Also some momentary formation of gas may have taken place and spalled the paste off by a weak explosive action. At any rate the loss of active material was undoubtedly responsible for the early failure of the cells as the base grid was intact.

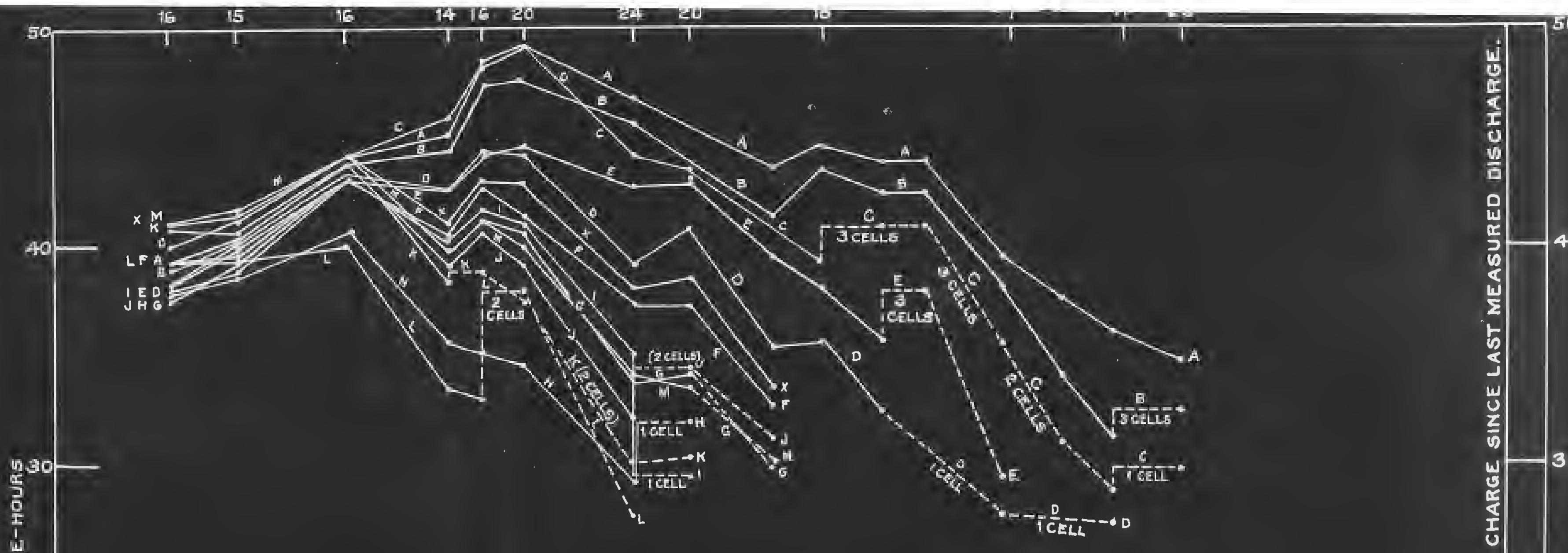
[redacted]

SUMMARY AND CONCLUSIONS

15. While the results of the current tests were largely inconclusive as far as establishing any single alloy as superior to types now in service, they may serve a directive influence for planning future work. It appears from physical tests and from the condition of several of the plates after dissembling the cells that satisfactory stability can be obtained in grids of the substitution alloy types without the high antimony now used. In fact, more experimental work will undoubtedly develop substitute alloys in which the antimony will be even less than 2-1/2%. The development of inhibitors such as cobalt or nickel to be used either in the electrolyte or in the paste for decreasing charging voltages would greatly increase the efficiency of cells made from substitution alloy grids. The cells of the subject series would undoubtedly have shown to better advantage under such conditions.

16. The cells made with 2-1/2% antimony plus 0.05% silver (B of plate 5) were the most promising of any of the present series. The comparable grid containing 0.10% silver with 2-1/2% antimony (C of plate 6) was also very good to 175 cycles when one of the cells failed. At the end of 265 cycles only one cell remained good, but the capacity was still high. From these results silver seems to be a promising substitute alloy for use in storage batteries when more is known about its influences. Some work has also been done by Mr. A. J. Dornblatt who was associated with the silver research project and who made and tested several alloys containing 4% antimony and varying amounts of silver. The results of this work will be available to the Laboratory very soon, as Mr. Dornblatt has promised to forward a copy of the work. This was presented to Columbia University as partial fulfillment of the requirements for Doctor of Science degree in 1940. Mr. Dornblatt has stated orally that his results indicate 0.10% silver to be extremely beneficial and somewhat better than either 0.05 or 0.15% of the element.

17. That more conclusive and valuable results were not obtained is due in part to lack of an intensive and comprehensive prosecution of the project with sufficient funds to make available the necessary manufacturing and testing equipment for a satisfactory program.



LIFE-TEST

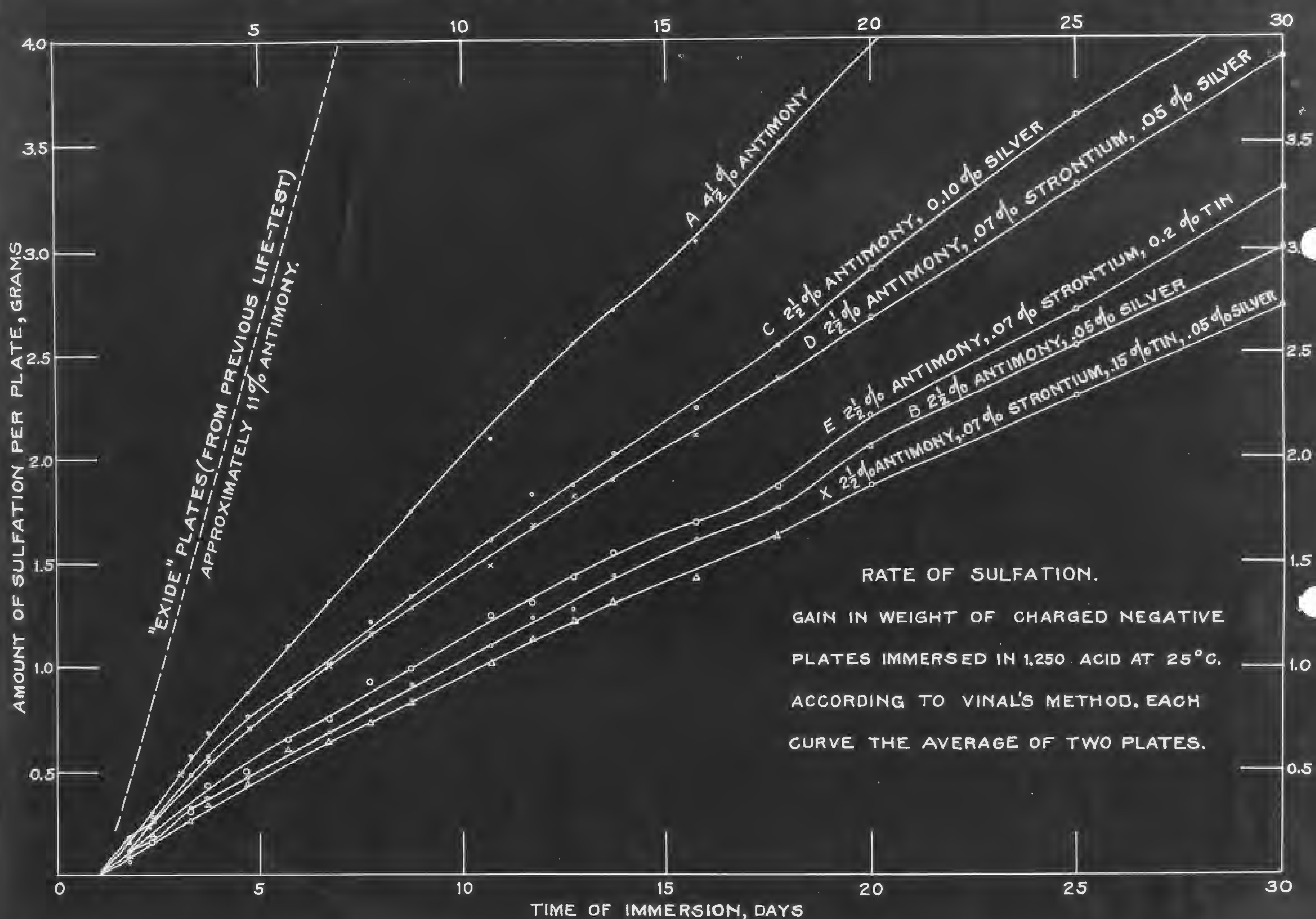
EACH LINE REPRESENTS THE HISTORY OF A GROUP OF FOUR SEVEN-PLATE CELLS, DOTTED LINES INDICATE THE REMOVAL OF ONE OR MORE CELLS FROM THE GROUP, THE ENDING OF A LINE THAT THE ENTIRE GROUP WAS REMOVED DUE TO LACK OF CAPACITY.

ALLOYS PREPARED AND GRIDS MANUFACTURED AT NAVAL RESEARCH LABORATORY.

PLATES PASTED, CELLS ASSEMBLED AND LIFE-TEST CONDUCTED AT THE NATIONAL BUREAU OF STANDARDS.

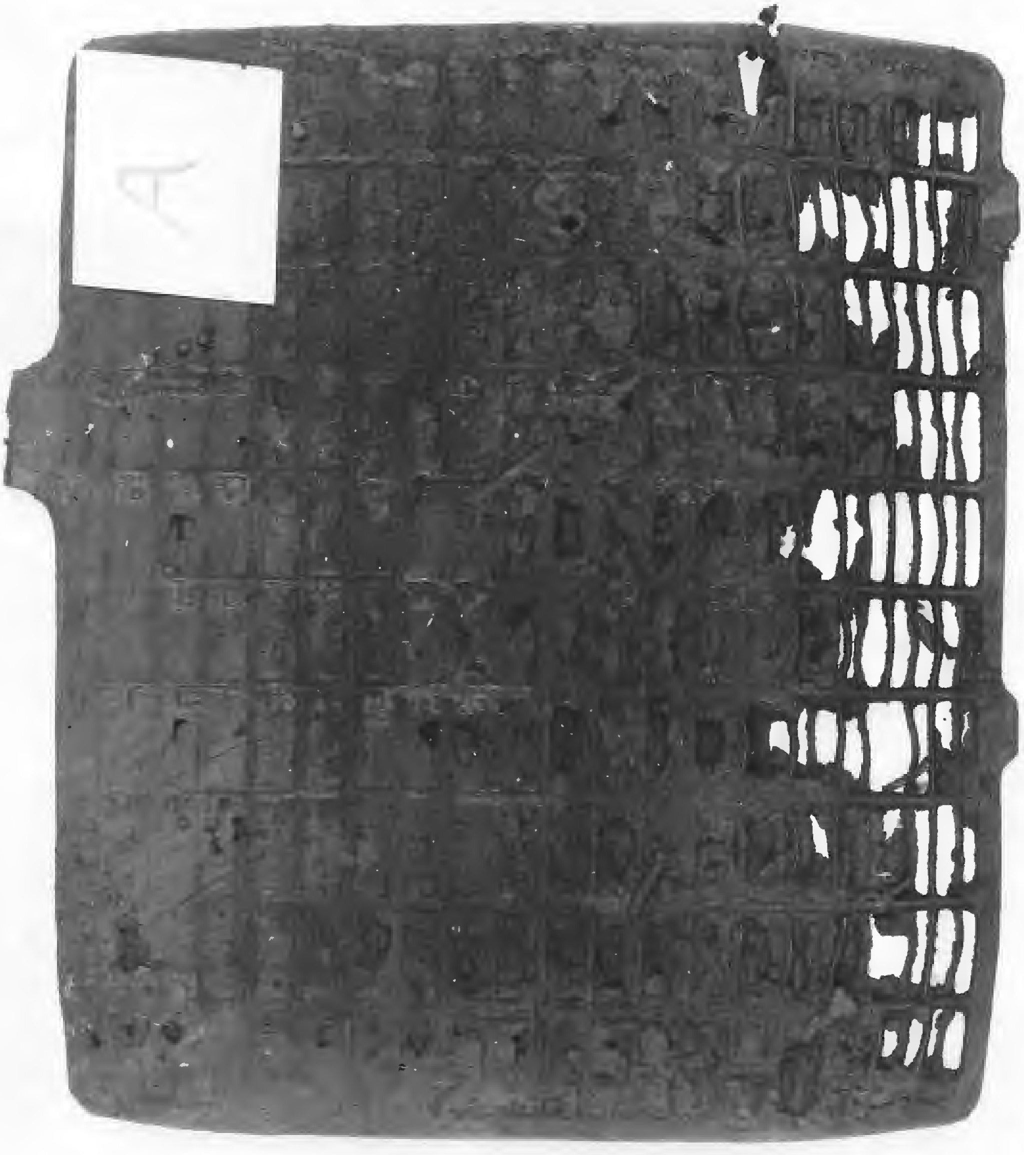
COMPOSITIONS, %					
ALLOY	ANTIMONY	STRONTIUM	TIN	SILVER	TELLURIUM
A	4½				
B	2½			.05	
C	2½			.10	
D	2½	.07		.05	
E	2½	.07	.20		
F	2½	.07		.10	
G	2½	.15		.05	
H	2½	.15	.20		
I	2½	.15		.10	
J	2½	.15	.15	.05	
K	2½	.15			.02
L	2½	.15	.20		.02
M	2½	.07	.40		
X	2½	.07	.15	.05	

PLATE I



"EXIDE" PLATES (FROM PREVIOUS LIFE-TEST)
APPROXIMATELY 11% ANTIMONY.
A 4½ % ANTIMONY
C 2½ % ANTIMONY, 0.10 % SILVER
D 2½ % ANTIMONY, .07 % STRONTIUM, .05 % SILVER
E 2½ % ANTIMONY, .07 % STRONTIUM, 0.2 % TIN
B 2½ % ANTIMONY, .05 % SILVER
X 2½ % ANTIMONY, .07 % STRONTIUM, .15 % TIN, .05 % SILVER
RATE OF SULFATION.
GAIN IN WEIGHT OF CHARGED NEGATIVE
PLATES IMMERSED IN 1.250 ACID AT 25°C.
ACCORDING TO VINAL'S METHOD. EACH
CURVE THE AVERAGE OF TWO PLATES.
AMOUNT OF SULFATION PER PLATE, GRAMS
TIME OF IMMERSION, DAYS

PLATE 2



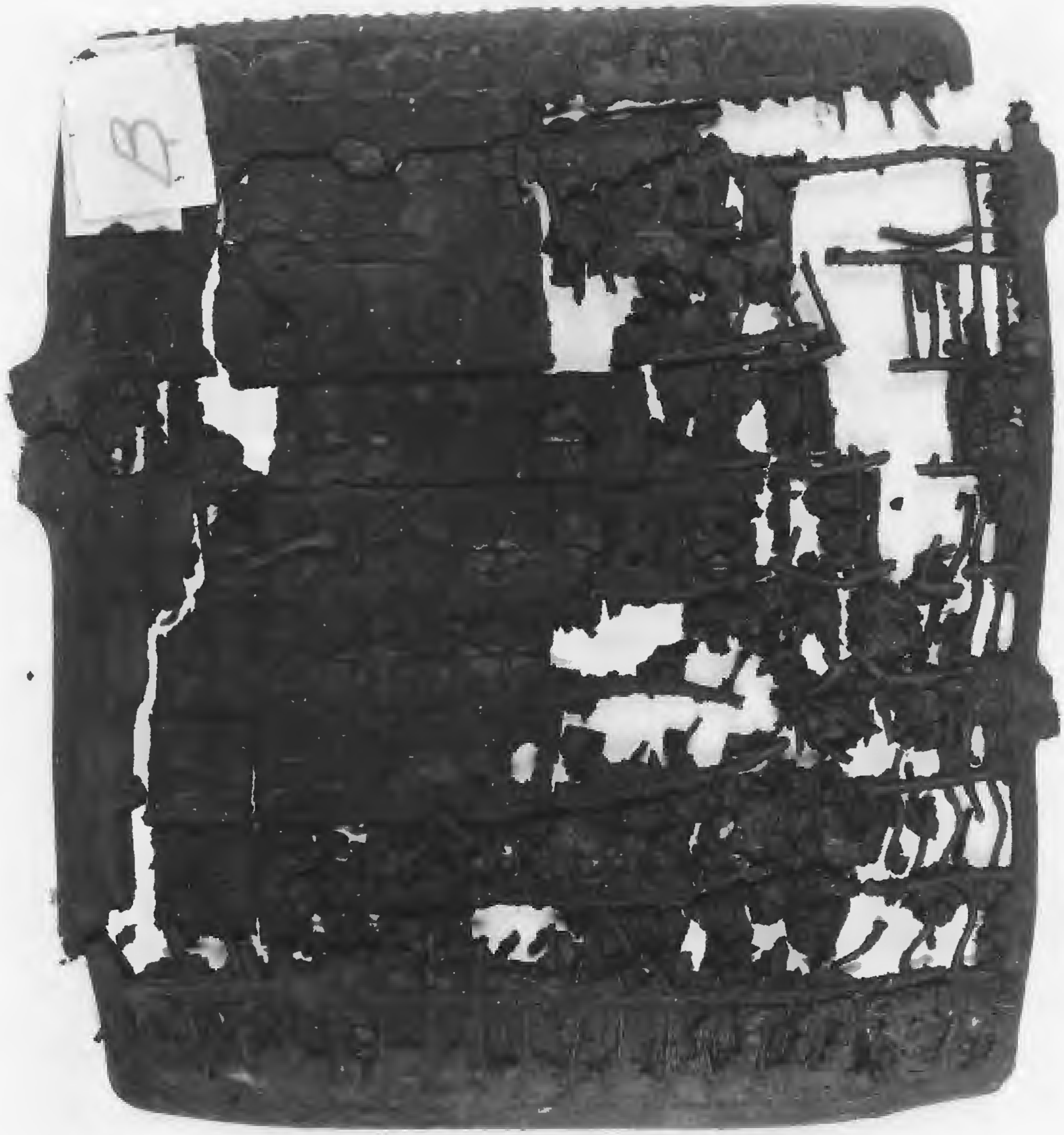


Plate 4

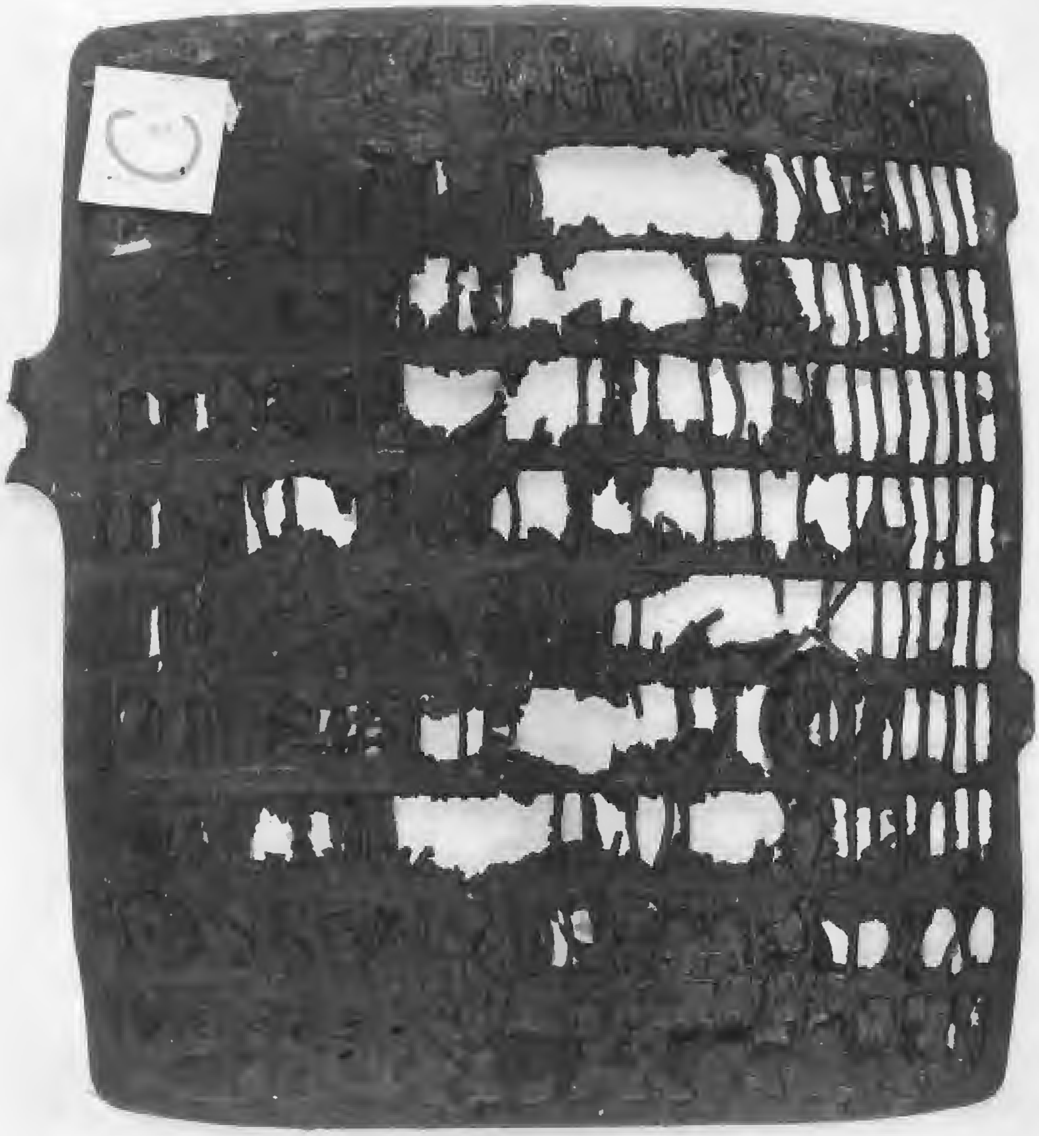


Plate 5

Plate 6

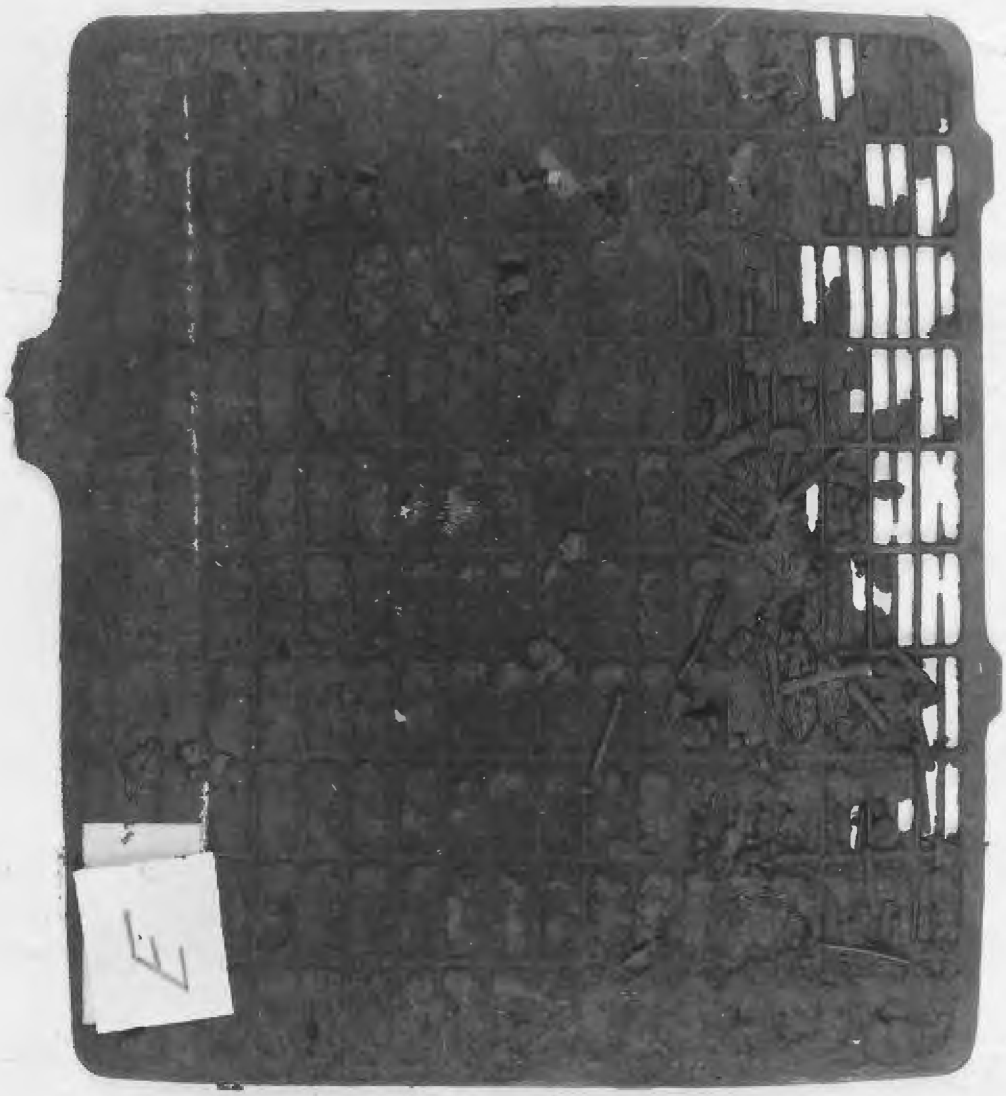


Plate 7

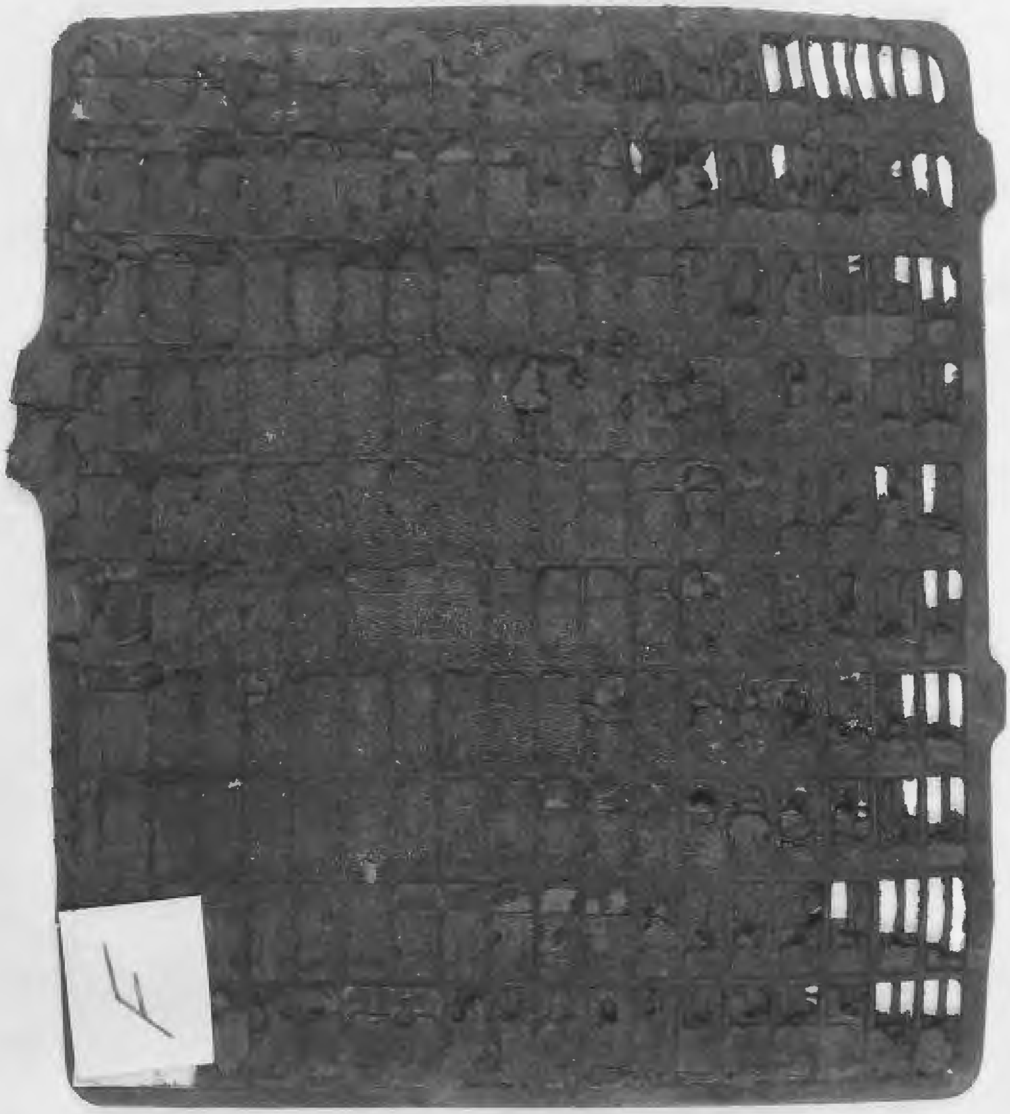


Plate 8

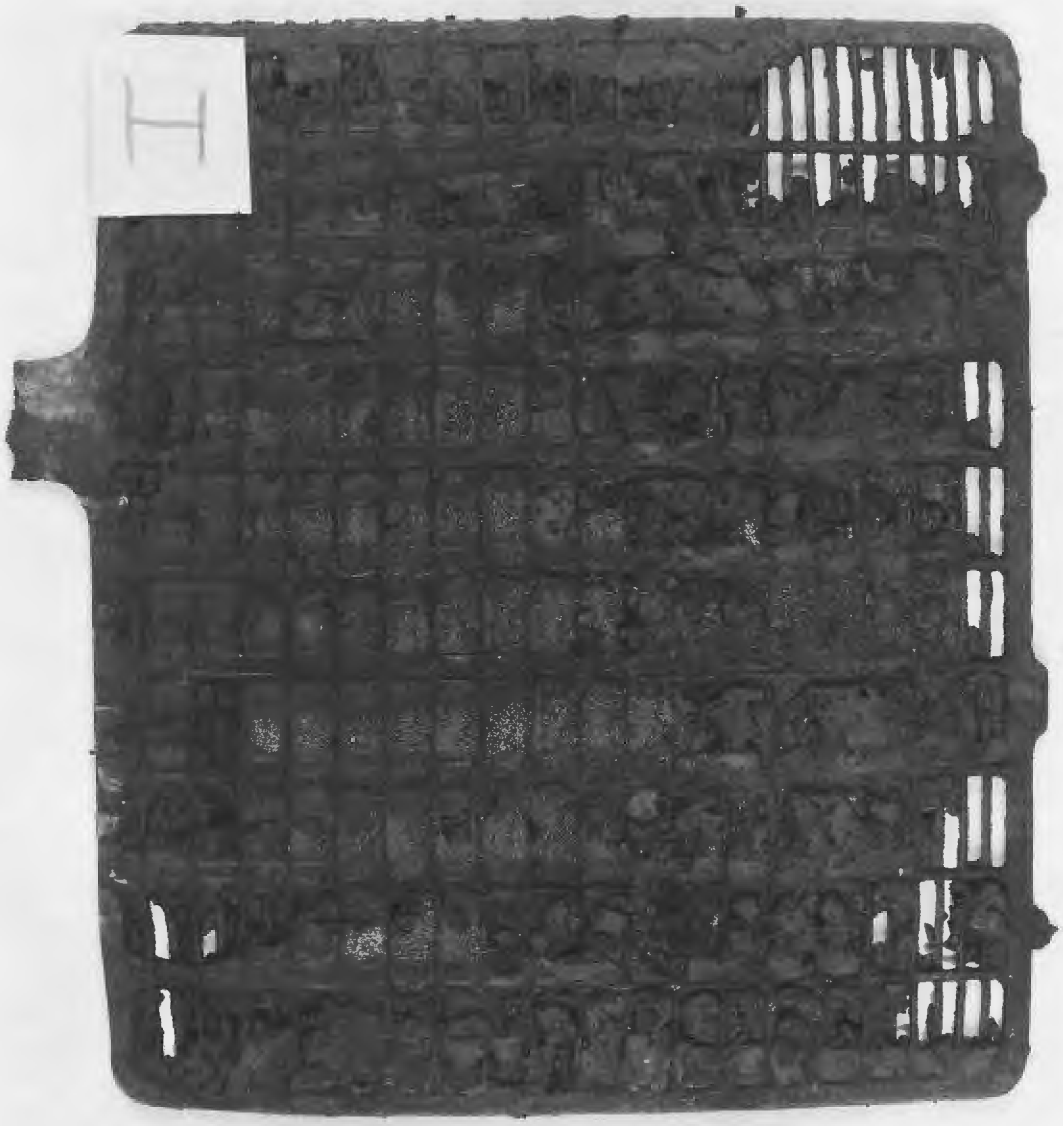


Plate 9

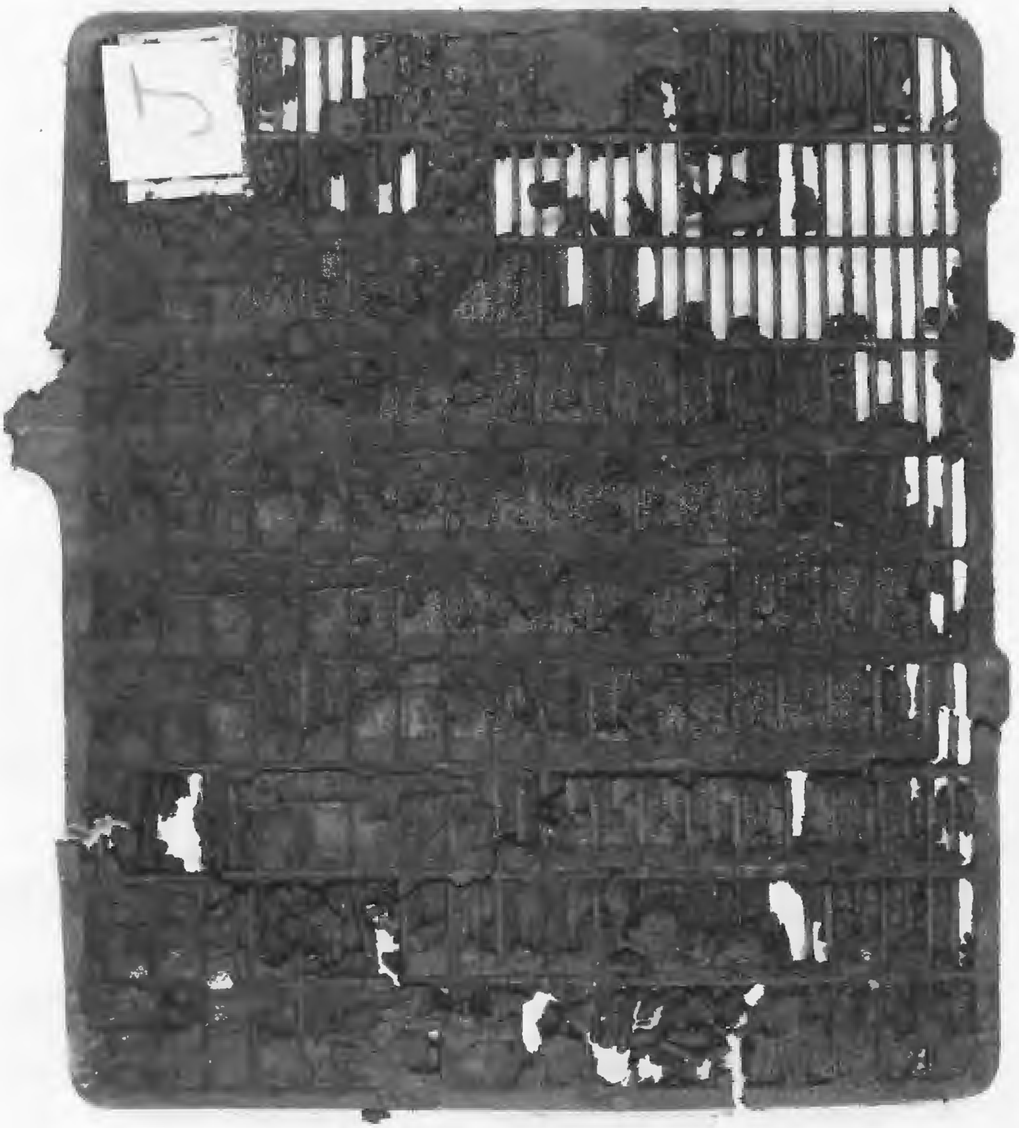


Plate 10

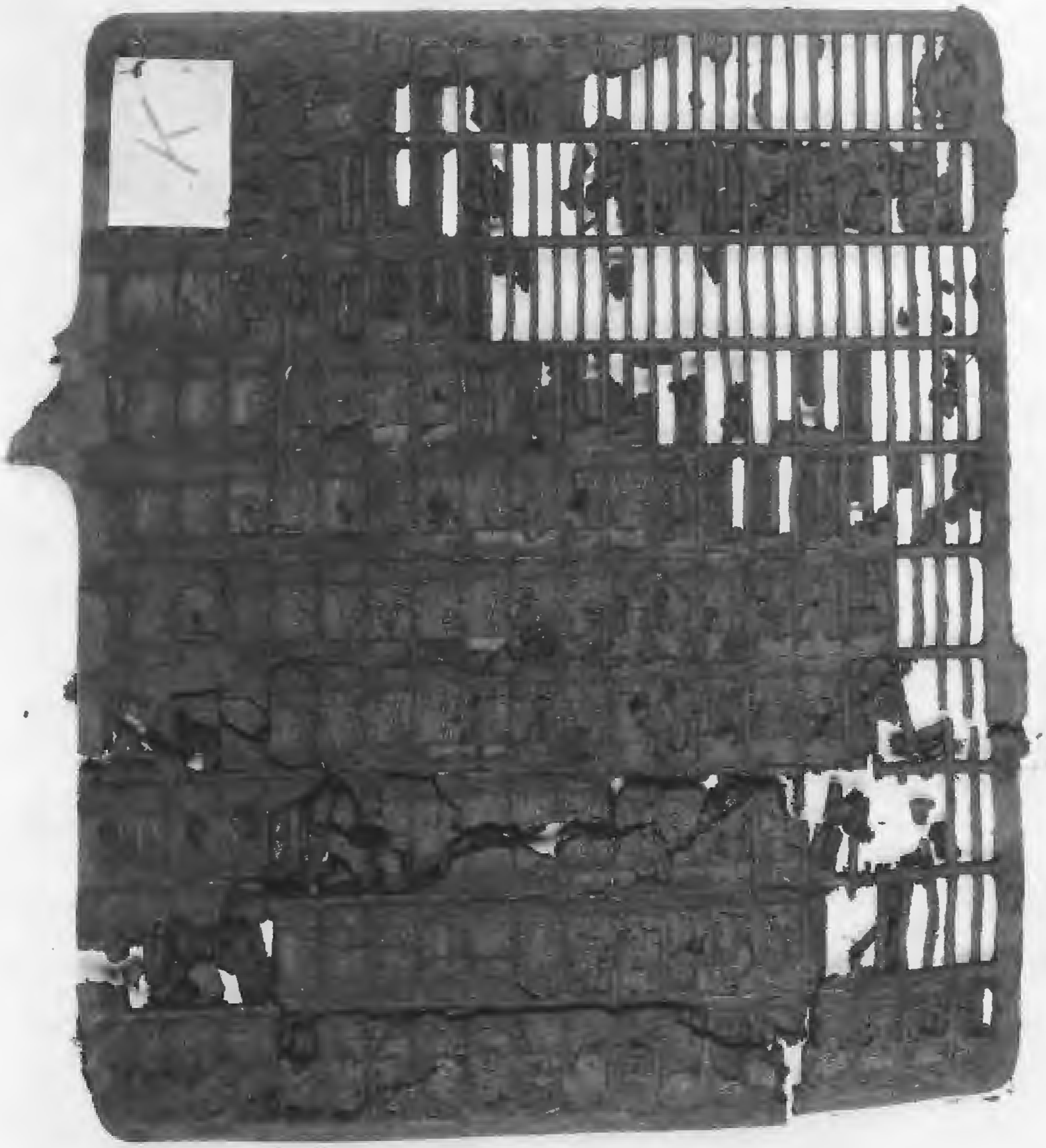


Plate 11

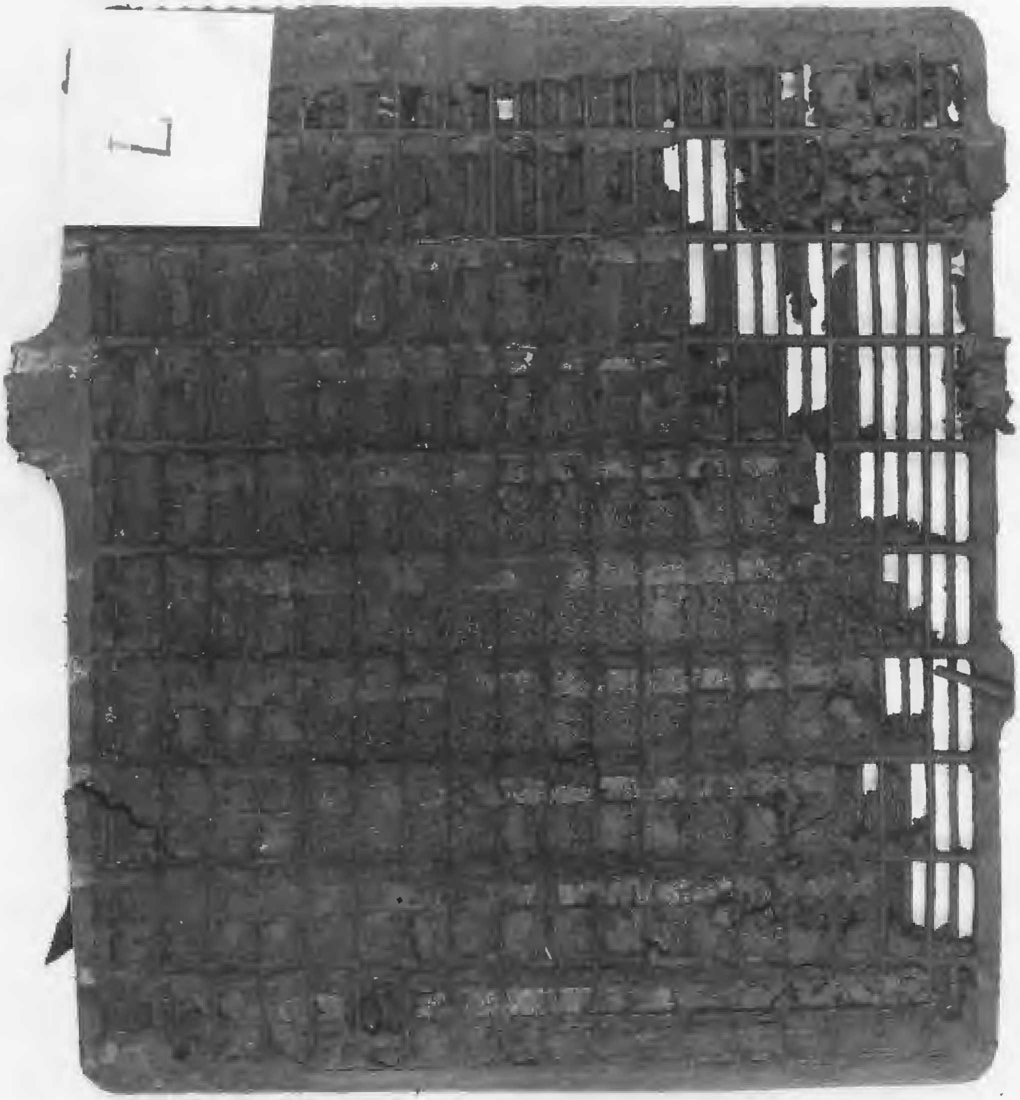


Plate 12

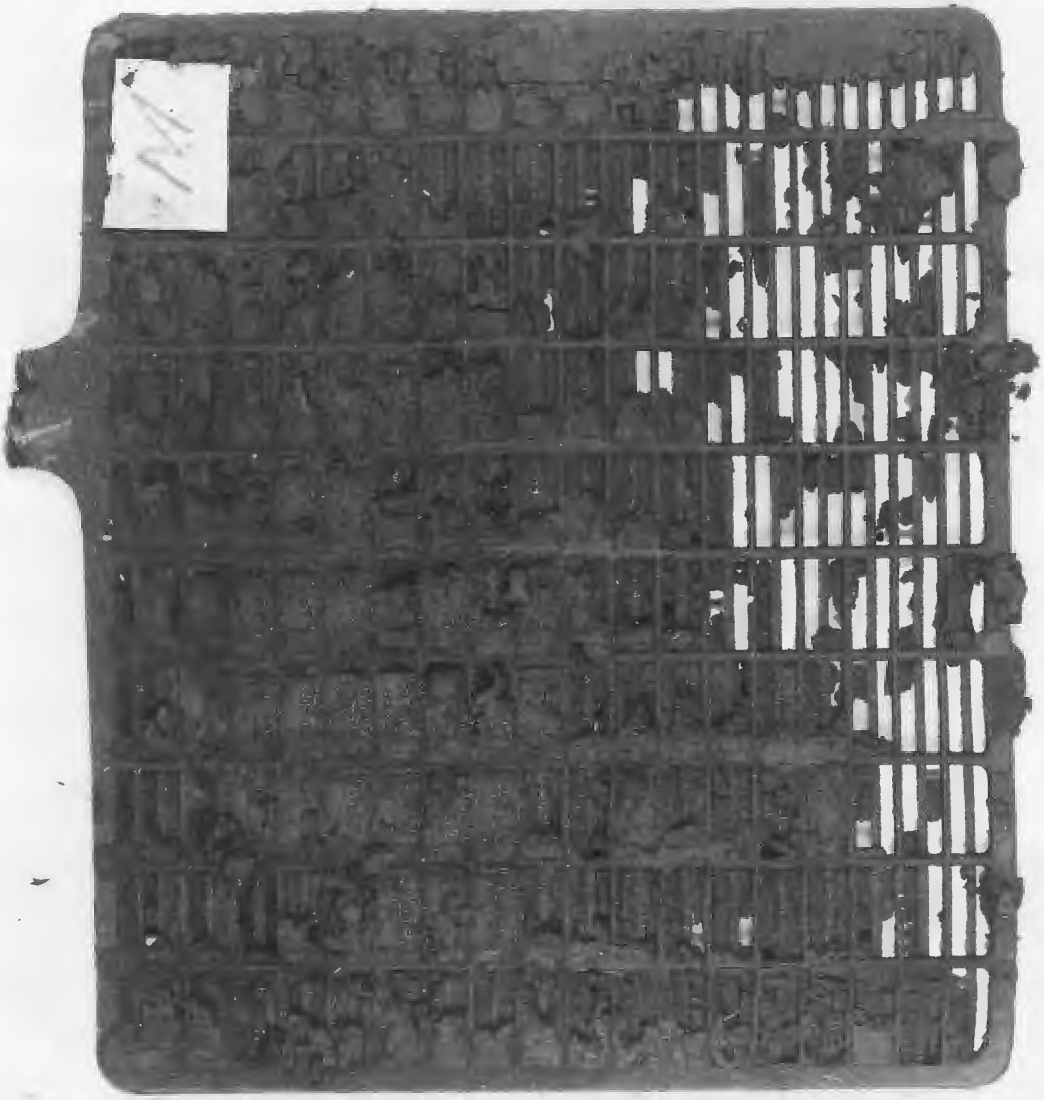


Plate 13

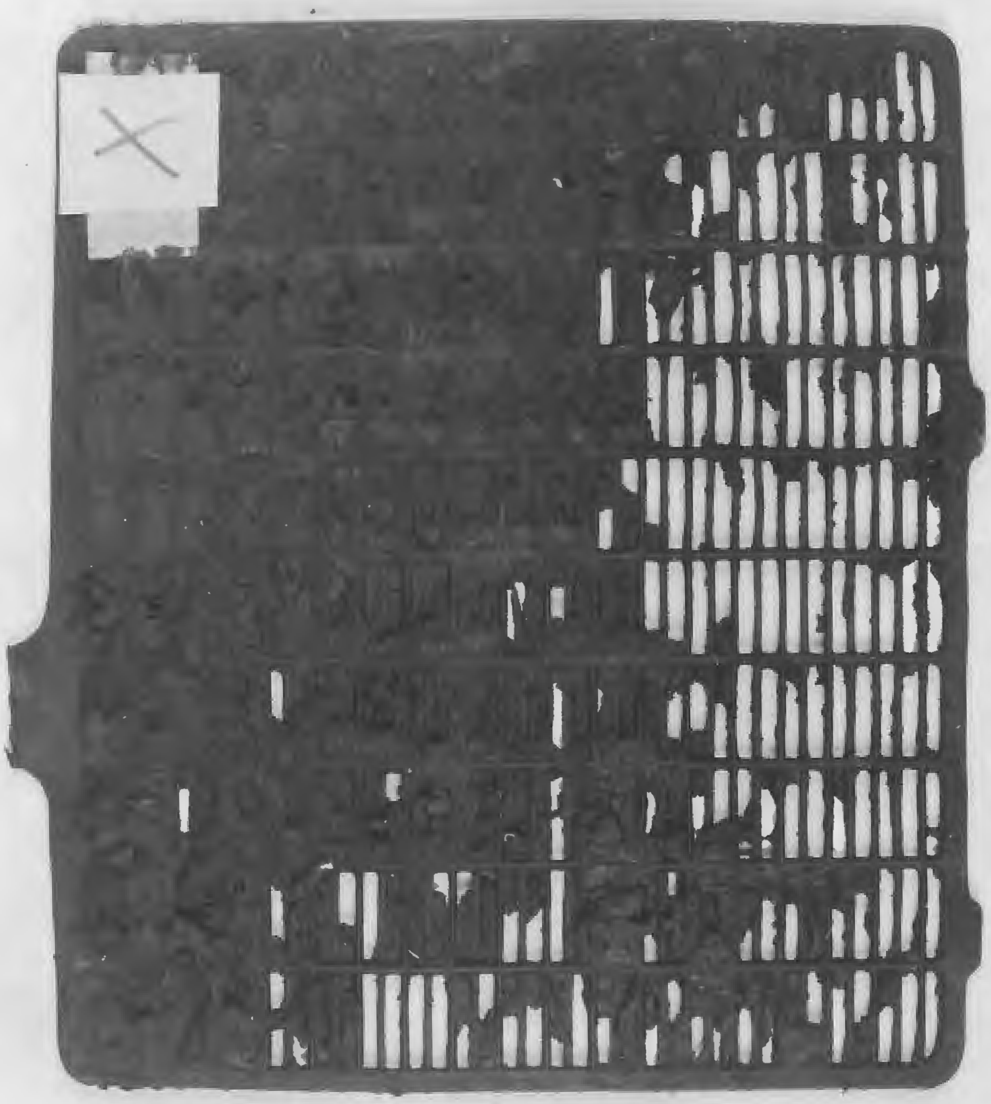


Plate 14