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Evaluation of A New Hardening Process for Steel Transfer Materials

I. J. Feinberg

Mechanical Properties Section
Metallurgy Division
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National Bureau of Standards
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Failure Analysis Report

May, 1976

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Mention of the name of a commercial process for the hardening of steel is in no way intended to imply an endorsement of the process by the National Bureau of Standards, nor is it intended to suggest that it is the best or only process to use for hardening steel. The process is identified in order to describe specifically what was done in this investigation.

Prepared for
Office of Engraving
Bureau of Engraving and Printing
Washington, D. C. 20234

U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, ***Secretary***
Edward O. Vetter, ***Under Secretary***
Dr. Betsy Ancker-Johnson, ***Assistant Secretary for Science and Technology***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Acting Director***

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SUMMARY

A new molten salt hardening process has been evaluated for hardening steels used in the three stage transfer process for printing stamps. Evaluation of the new process was undertaken because virtually all cyanide salts are eliminated as ingredients in the process. It was found that complete elimination of cyanide emissions is not achieved in the new process, however, the level of cyanide emitted does meet OSHA requirements. A case-hardening capability was exhibited in experimental tests on Bureau of Engraving and Printing materials, but case depths and hardness did not meet Bureau of Engraving and Printing requirements. Further development of the new process is needed before it can be considered for the Bureau of Engraving and Printing.

1. INTRODUCTION

Cyaniding of steel transfer materials (dies, rolls, transfer plates) has been employed by the Office of Engraving of the Bureau of Engraving and Printing (Bu E&P) for many years. Cyaniding has been adapted to both case and through hardening of selected steel materials used in the three stage transfer process for printing stamps and has been found to be consistently satisfactory in these applications. Nevertheless, Bu E&P has deemed it advisable to investigate the practicability of shifting to some other hardening process, because of a concern with health hazards, and has requested an NBS investigation of such processes. The investigation of one substitute process is reported herein. [1]*

1.1 Some Requirements of a Substitute Hardening Process

The following may be considered as requirements for a suitable replacement process.

a. Freedom from cyanide toxicity.

b. Capability of obtaining acceptable case hardnesses and case depths for components austenitized at 1450F to 1600F, the temperature range in which presently-used transfer process steels are austenitized.

c. Capability of the equipment used to accommodate the dimensions and the configurations of the material to be hardened.

d. Adequate protection of engraved surfaces from damage.

e. Cleanliness of material surfaces after hardening and a good product from an engraver's standpoint.

f. Acceptable costs of the initial installation and of subsequent operation from the standpoint of a small production output.

1.2 Possible Substitute Processes

Consideration was given to the following as substitute hardening processes:

a. Gas carburizing [2a]

b. Pack carburizing [2b]

c. Gaseous atmosphere carbonitriding [2c]

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* Figures in brackets indicate references at the end of this report.

d. Induction hardening [2d]

e. Flame hardening [2e]

All of the processes listed above were reviewed and found to involve the installation of costly new equipment and extensive shut down time during installation. Thus, they were given limited consideration. An interest was found in a newly developed molten salt hardening process [1 This hardening process appeared to be adaptable to the case-hardening of the transfer process materials currently hardened by cyaniding at Bu E&P. Moreover it appeared to require less expensive equipment for a change-over than that needed by other replacement processes.

1.2.1 Description of the New Hardening Process

The salt bath used in the new case hardening procedure is prepared from three ingredients named by the manufacturer as follows:

a. NOCY base salt

b. LOCYN pellets

c. NOCY additive

A detailed description of the composition of the ingredients was not available from the manufacturer for proprietary reasons. However, the manufacturer explained that the NOCY base salt is composed of carbonates and chlorides, the LOCYN pellets have an organic base and are high in nitrogen and the NOCY additive is synthesized graphite. According to the manufacturer, graphite reacting with sodium carbonate, $Na_2 CO_3$, in the bath forms carbon monoxide, CO, which is the active carburizing agent. Nascent nitrogen, N, entering the case is derived from breakdown of the LOCYN pellets.

Salt pot equipment such as that used for cyaniding at Bu E&P is suitable for hardening by the new process. However, provision must be made for stirring (agitation) of the molten salt bath during the hardening operation. The process was reported by the manufacturer to be suitable for operation at temperatures of 1450 to 1600F, the range at which hardening is done at Bu E&P.

This report gives results of an NBS evaluation for Bu E&P of the new process applied to the hardening of steel transfer materials.

2. PURPOSE

Purposes of this investigation were to learn characteristics of the new process and to determine its suitability as a replacement for the molten cyanide salt process currently used in heat treating transfer materials at the Bureau of Engraving and Printing by performing laboratory tests on these materials. A requirement in heat treating is operation at a temperature range of 1450 to 1600F at which certain materials are case-hardened and others through hardened.

3. EXPERIMENTAL WORK

Experimental work included heat treatment of transfer process test material supplied by the Bu E&P. The treatments were carried out at the heat treating laboratory of the manufacturer in Detroit, Michigan and at NBS in Gaithersburg, Maryland. Case depth and hardness determinations were made. Metallographic examinations were conducted to determine the effects of the hardening procedure on case and core microstructures.

Replenishment of salt pot additions necessary for continuous salt bath operation was studied. Tests were conducted under the direction of the NBS Air and Water Pollution Section to determine whether toxic cyanide fumes were evolved during hardening.

3.1 Materials

3.1.1 Characteristics of Transfer Process Components

Dies - Dies are engraved in the first stage of the transfer processes. A modified AISI 1045 steel is specified for transfer dies. The dies are flat plates with dimensions of 0.25 inch x 4.00 inch x 4.50 inch. One surface of a die plate is polished. After engraving on the polished surface, die plates are through hardened with the intention of achieving a desired hardness of 80 HR30N on the polished, engraved surface with a tolerable gradient to about 77 HR30N at a depth of 0.006 inch from this surface.

Rolls - In the second stage of the transfer process rolls are revolved over dies to "pick-up" impressions from the engraving on the dies. Rolls are presently made from W2 tool steel because AISI 1031, a preferred material, is currently unavailable for this application. The rolls are 2.75 inch in diameter by 1.125 inch in length, have a tapered drilled hole at the center and a polished cylindrical surface. After pick-up of impressions on the cylindrical surface, the rolls are heat treated to obtain a case 0.004 inch to 0.006 inch deep adjacent to the cylindrical surface, with a hardness of 80 HR30N on the roll surface.

Transfer Plates - In the third stage of the transfer process, impressions on rolls are transferred (rolled) onto the finely polished surfaces of transfer plates. Transfer plates are presently made from AISI 1030 steel (AISI 1031 modified, when available. Transfer plates start as flat pieces with dimensions of 0.25 inch x 19.5 inch x 24.5 inch. After transfer of impressions on the rolls to the polished surface of the transfer plates, the plates are reduced to a thickness of 0.180 inch by grinding the opposite surface of the plates. Next, the plates are shaped into half cylinders of 6.5 inch radius. Heat treatment follows to produce a hardness of 77 - 80 HR15N* on the impressed polished surface of the plates and a case with a depth of 0.004 inch to 0.006 inch adjacent to this surface.

3.1.2 Experimental Test Material

Tests were conducted on 0.25 inch x 1.0 inch x 1.0 inch specimens cut from AISI 1031 and AISI 1045 steel transfer process plates, supplied by the Office of Engraving of the Bu E&P. Tests were also conducted on small wedge-shaped specimens cut from W2 tool steel rolls, also supplied by the Office of Engraving. Each roll was cut to provide 10 specimens. Given below in section 3.1.2.1 are property data obtained for specimens 1031-5, 1045-6 and W2-6. These data are considered to be representative of that for all test specimens of a similar composition.

3.1.2.1 Chemical Analysis of Test Material, As-received

The chemical composition of samples of as-received test material as determined from analyses by spectrometric or combustion methods are given in Table 1.

Table 1. Chemical Analysis of Test Material, As-Received

		Samples	
	1031-5	1045-6	W2-6
Carbon	0.33%	0.46%	1.06%
Manganese	0.53	0.10	0.31
Phosphorus	0.005	0.005	0.006
Sulfur	0.013	0.007	0.008
Silicon	0.21	<0.05	0.25
Nickel	<0.05	0.05	0.05
Chromium	<0.05	0.08	0.10
Molybdenum	<0.05	<0.05	<0.05
Copper	<0.05	<0.05	<0.05
Vanadium	--	--	0.18

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* HR15N is the accepted ASTM notation for hardness on the Rockwell 15N scale.

3.1.2.2 Hardness of Test Material, As-Received

The hardness obtained on specimens of the as-received test material are given in Table 2.

Table 2. Hardness of Test Material, as-received

Area	Hardness of Specimens 1031-1	 1045-1	 W2-1
Polished face	77 HRB*	77 HRB	64 HRB
Longitudinal edge	74 HRB	75 HRB	-
Transverse edge	74 HRB	74 HRB	85 HRB**

3.1.2.3 Microstructure of Test Material, As-Received

The microstructures of specimens 1031-1, 1045-1 and W2-1, as received, are shown in Figures 1a, 1b and 1c, respectively, and are described in the legends for these figures.

4. TEST PROCEDURES

4.1 Test Equipment

4.1.1 Equipment Used at Manufacturer's Plant

Specimens were heated for hardening at the manufacturer's plant in a cast iron pot having an inside diameter of approximately 9 inches and a depth of approximately 12 inches. Electric power served as a heat source. A thermocouple was inserted in the pot during operation and temperatures were monitored on the laboratory console. Salts in the pot were stirred by a 3.5 inch diameter propeller driven by an air motor. Figure 2 is a schematic representation of the salt pot and stirrer arrangement. After hardening, specimens were tempered in a convection type tempering furnace.

4.1.2 Equipment Used at NBS

At NBS specimens were heated for hardening in a cast iron pot, 6 inches in diameter by 12 inches deep; also using electric power

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* HRB is the accepted ASTM notation for hardness on the Rockwell B scale.

** Value is for a reading obtained at a depth of 0.25 inch normal to the cylindrical polished surface of this W2 roll specimen. W2-1 contained a decarburized zone approximately 0.005 inch deep adjacent to the cylindrical polished surface. In this zone, the hardness ranged from HRB 42 at 0.002 inch to HRB 76 at 0.005 inch from the polished surface. All W2 rolls supplied have a decarburized surface zone.

as a heat source. Temperature readings were obtained from a fixed thermocouple inside the salt pot and monitored on the laboratory console. Temperatures were also observed, for greater accuracy, from potentiometer readings obtained from an auxiliary thermocouple inserted in the pot during operation. Figure 3 is a view of equipment used in the NBS case-hardening tests. A recirculating air furnace was used in tempering.

4.2 Preparation of a Salt Bath

The following is the manufacturer's recommended procedure for preparation of salt baths that was used in all hardening evaluation tests.

a. Fill base salt, which is in powder form, to near the top of the pot, weighing the amount added. Melt down at 1700F.

b. With the temperature still at 1700F add the NOCY additive, which is in powder form, stirring until a foamy cover is attained. Record the weight of additive supplied. Use a wire test* to determine whether case hardening is attained. More of the additive is required if hardening is not attained. Drop the temperature to 1500F after hardening is achieved.

c. Add LOCYN pellets equal to 2 1/2 percent by weight of the base salt additive mixture. Use a wire test to determine whether case hardening is obtained. If the wire test is negative, more of the pellets are required.

4.3 Experimental Hardening Procedure Variables

Initially, the standard treatments for hardening at Bu E&P were followed quite closely with respect to temperature, holding times and quenchants. Later, certain modifications in these factors were found to be desirable. A superficial hardness test on a polished surface was used as a control in determining whether a given procedure was suitable. When the hardness was found to be unacceptable, the procedure was modified in the test that followed. The condition of polished surfaces was closely observed and the procedure was also modified if the appearance of a polished surface after hardening was considered to be unsatisfactory. Criteria resulting in modification were the presence of an adherent black deposit and/or extensive staining on the polished surface of a specimen after hardening. Sixteen AISI 1031, thirteen AISI 1045 and four W2 specimens were hardened in the course of the investigation. Hardening procedures employed for selected specimens are described in the descriptive information with Figures 6 through 23.

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* The wire test involves the insertion of a 16 or 18 gage mild steel (AISI 1010 or 1015) wire into the molten salts for one-half hour. After quenching the heated end of the wire in water, case-hardening is indicated if this end will break in a brittle manner before it can be bent back 180 degrees on itself.

4.4 Analysis of Exhaust Air from the New Hardening Process

A test for cyanide released into the exhaust air during hardening was conducted by the NBS Air Pollution and Analysis Section. Details of the procedure used in the analysis and results obtained are given in an analytical report entitled "The Sampling and Analysis for Cyanide in the Exhaust Air from a Steel Hardening Process," which is included as an Appendix to this report. Equipment used in the exhaust air analysis is shown in Figure 4.

5. RESULTS AND DISCUSSIONS

5.1 Chemical Composition of As-Received Material

The chemical composition of the AISI 1031 sample, which was analyzed, complied with the requirements in the Bu E&P Specification for Steel Engraving Plates, dated December 17, 1970. The 0.10 manganese content of the AISI 1045 sample is lower than the 0.60 to 0.90 percent manganese content specified for this material. The composition of the W2 sample is similar to that required for AISI W2. The chemical analyses confirmed that the compositions of the materials used in the NBS evaluation tests are the same as those used in Bu E&P production runs.

5.2 Hardness Characteristics of Heat Treated Material

The hardness of polished surfaces and the hardness variations observed in microhardness traverses conducted on specimens after heat treatment are given in Table 3 for selected AISI 1031 specimens, in Table 4 for selected AISI 1045 specimens and in Table 5 for selected W2 specimens. The traverses were made on a Tukon hardness tester using a Knoop indenter and a 500 gram load. Indentation measurements were made using a 20 X objective. Rockwell HR15N or HR30N hardness values given are the approximate equivalent values derived from Knoop hardness numbers (KHN). Knoop hardness readings were made at 0.001 inch intervals starting at 0.001 inch from the polished surface and continuing into the thickness of each specimen. Tables 3, 4 and 5 give only the hardnesses observed in cases to a maximum depth of 0.004 inch, which is considered to be sufficient in evaluating the depth of hardening capability of the new process in relation to Bu E&P requirements.

An acceptable polished surface hardness and acceptable case hardness and depth of case were sought in the experimental hardening tests. The selected hardness test results given in Tables 3, 4 and 5 are considered to be representative of results attained in these tests. Table 3 shows that the polished surface hardness of one

AISI 1031 specimen after hardening was considerably higher than required, one was within the required hardness range and the rest below. The surface hardnesses of the AISI 1045 specimens were all lower than the required hardness. A high surface hardness was obtained on one W2 specimen while that of the others was lower than required.

Most of the AISI 1031 specimens exhibited acceptable hardness values in case areas immediately adjacent to polished surfaces, as shown in Table 3. However, the cases were shallow with hardness generally decreasing rapidly to unacceptable values with increasing distance from the surfaces. The hardnesses obtained in the cases of the AISI 1045 specimens were all lower than that required. The cases in the AISI 1045 specimens did not exhibit the marked hardness gradients observed in the cases of the AISI 1031 specimens. Insufficient hardness was obtained in the cases of the W2 specimens.

5.3 Condition of Polished Surfaces After Hardening

The surfaces of specimens hardened at the manufacturers laboratory were clean after hardening. However, some of the specimens hardened at NBS had a black, adherent coating after hardening. The coatings observed on the polished surfaces of hardened specimens 1031-14 and 1045-12 are shown in Figures 5a and 5b, respectively. It was found that the coatings could be removed by immersion of the specimens in a 10 percent solution of sulfamic acid (NH_2SO_3H) at room temperature for from fifteen to thirty minutes, followed by swabbing with a soft bristle brush and a clear water rinse. The appearance of the polished surfaces of hardened specimens 1031-14 and 1045-12 after the sulfamic acid cleaning treatment are shown in Figures 5c and 5d, respectively. The black, adherent coating was observed on some of the specimens with low surface hardness reported in 5.2. It is uncertain as to whether the coating formed on specimens while they were in the salt bath; or was picked-up by specimens from a residual, substance on the surface of the bath, when specimens were being removed for quenching.

5.4 Case and Core Microstructures Obtained In Experimental Tests

Figures 6 through 22 contain photomicrographs showing the structures of representative specimens hardened in the experimental hardening tests. Hardening procedures and microstructures are described in the figure legends.

5.4.1 Observation of Microstructures of Hardened AISI 1031 Specimens

Fine grained cases varying in depth from 0.003 inch to 0.006 inch were observed adjacent to the polished surfaces of hardened specimens. The cases were followed by a coarser structural transition zone and finally by the core which had the coarsest structure. The cases of specimens 1031-2, 7, 8, 11 and 15, which were oil quenched in hardening, contained tempered martensite with ferrite in the grain boundaries and in the transition zones. The cores of these specimens contained ferrite in a matrix of tempered martensite. The microstructures of the case, transition zone and core of specimen 1031-9, Figure 10, which was brine-quenched in hardening, appeared to be predominantly tempered martensite. The variation in austenitizing temperatures of oil quenched specimens, ranging from 1550F to 1575F, and the variation in holding time at temperatures ranging from 36 to 45 minutes, produced no apparent effect on case and core structures. The case depths of oil quenched AISI 1031 specimens were apparently unaffected by variation in hardening temperature or time at temperatures. No increase in case depths through the use of fresh salt baths or salt replenishment was observed metallographically.

5.4.2 Observation of Microstructures of Hardened AISI 1045 Specimens

Specimens were austenitized in the salt bath at temperatures ranging from 1480F to 1550F and generally held in the bath for 30 minutes. All of the AISI 1045 specimens were quenched in brine. Tempered martensite predominated in the three structural zones of these specimens. Troostite was observed at high magnification in grain boundaries in the cores of all hardened 1045 specimens. Case depths, observed metallographically, ranged from 0.003 inch to 0.004 inch. Variations in the austenitizing temperature or salt bath replenishment had little effect on case depths.

5.4.3 Observation of Microstructures of Hardened W2 Specimens

W2 specimens were austenitized in the salt bath at temperatures ranging from 1500F to 1575F and held in the bath for 60 minutes. All of the W2 specimens were quenched in brine. All exhibited a five-grained structural transition zone between case and core. The cases contained carbides in a ferrite matrix while cores were essentially tempered martensite. The structures in transition zones were mixed, containing some ferrite and carbide particles and tempered martensite. Case depths, observed metallographically, ranged from 0.003 to 0.006 inch. No apparent affect on case depths from salt bath replenishment was observed.

6. CONCLUSIONS

The two principal criteria in judging the suitability of a process to be substituted for the cyanide hardening process currently in use are considered to be (a) freedom from cyanide toxicity and (b) capability of obtaining acceptable component case hardness and case depth.

With regard to cyanide toxicity, the analyses described in the appendix were conducted on samples of the base salt, additive and pellet ingredients used in the process. Analyses were conducted on samples of quench water. The air above the salt pot was analyzed for cyanide emissions from the molten salts in the pot during operation of a hardening test. This air which is vented from the salt pot during operation of hardening tests is hereinafter referred to as exhaust air.

As reported in the appendix, no cyanide was found in the base salt or in the additive. Cyanide, 0.004 percent by weight, found in a pellet sample, can be considered to be a trace contaminant.

Quench water analyzed after the hardening tests was found to contain 3.4 mg. of cyanide in 2500 ml. of quench water. This relatively high concentration of cyanide in the quench water was evidently derived from molten salts adhering to specimens that were quenched. Avoidance of physical contact with the quenchant would be desirable. The dangerous cyanide radical in the quenchant can be rendered harmless by the controlled addition of chlorine or sodium hypochlorite into the quenchant, using suitable precautions [3].

Cyanide, 0.17 parts per million, was found in the exhaust air in one of the four sampling periods during the hardening test described in the appendix. This amount is less than 2 percent of the OSHA permissible concentration level for HCN in an eight hour day. The appendix speculates that no cyanide is emitted into the exhaust air in gaseous form, but that the cyanide is most likely in a particulate state.

It is further speculated that cyanide in the concentrations reported in the Appendix, may be derived from a chemical reaction of the ingredient salts during hardening.

The new process exhibited a hardening capability for all three materials of interest, as demonstrated by comparing hardnesses in Table 2 with hardnesses in Tables 3 through 5. Hardness tests and microstructural examination revealed the formation of cases adjacent to the polished surfaces of specimens. It seems that the case hardnesses observed stem from two interrelated factors: (1) The fundamental hardness increase resulting from quenching from austenitizing temperatures; (2) The diffusion of carbon and nitrogen from the hardening salts. The diffusion of carbon into specimens is indicated by the increased martensite content in case areas. It is assumed, because of the nitrogen content of the salts, that there was also some diffusion of nitrogen into the cases although there was little microstructural evidence of this. The hardness obtained in a case is significantly greater in carbonitriding where nitrogen is added, than when the same steel is carburized only [4].

Oil quenching resulted in the presence of ferrite in the grain boundaries of the AISI 1031 specimens. The ferrite evidently contributed to the low case hardness. Too slow a cooling rate, evidenced by troostite in core grain boundaries, may account for the generally low case hardness of the AISI 1045 specimens. Low case hardness of W2 specimens may be attributed to an insufficient diffusion of carbon and possibly nitrogen into the decarburized zones of these specimens. As stated earlier in this report W2 rolls, as received, contain a decarburized zone adjacent to their cylindrical surface.

The holding time and temperatures levels employed for case hardening, in the currently used cyanide process at Bu E&P, suffice to provide adequate case depths and hardness. However, in applying these levels in experimental tests of the new process, shallower cases and lower case hardnesses were obtained. It may be that the ingredients used in the new process do not respond, at these levels, to provide an adequate supply of carbon and nitrogen for a sufficient case. Case compositions and depth could possibly have been improved by longer times at temperature and/or higher temperatures plus added agitation. However, higher temperatures or longer holding times in these tests could have led to serious grain growth or other microstructural changes deleterious to the mechanical properties of the hardened steels.

From observations made in this investigation, the new process appears to have some potential as a substitute for currently-used cyaniding processes. It was demonstrated that the process has a case-hardening capability and that cyanide toxicity is not a matter of great concern. The question as to the nitriding efficacy of the process in case-hardening merits further investigation and probably further development.

7. RECOMMENDATIONS

Evaluation tests at NBS were made in a small salt pot, with small specimens and with perhaps inadequate bath agitation. Further evaluation tests might involve larger salt pots, more sophisticated bath agitation and test material approaching the size of the material case hardened at Bu E&P.

ACKNOWLEDGEMENT

The author wishes to express his appreciation for the helpful information supplied during the investigation by Walter Olson and Paul Krasley of the Office of Engraving of the Bureau of Engraving and Printing. Thanks are due to Dr. Bruce Christ, Acting Chief of the NBS Mechanical Properties Section, for helpful suggestions. Leonard C. Smith of the Mechanical Properties Section obtained the hardness data and prepared the metallographic illustrations.

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[1] LOCYN Process, Park Chemical Co., 8074 Military Ave., Detroit, Michigan 48204, developer and manufacturer.

[2a through 2e] ASM Metals Handbook, Vol. 2, 8th Edition, 1964, American Society for Metals, Metals Park, Ohio 44073.

[2a] Gas Carburizing, p. 93.
[2b] Pack Carburizing, p. 115.
[2c] Gaseous Atmosphere Carbonitriding, p. 119.
[2d] Induction Hardening, p. 167.
[2e] Flame Hardening, p. 189.

[3] Cyanide, Wastewater Control and Treatment, A. Edward Ward, Electroplating Engineering Handbook, 3rd Edition, A. Kenneth Graham, Editor, Van Nostrand Reinhold Co., publisher, New York, N.Y., 1971, p. 357.

[4] Hardenability of Case, ASM Metals Handbook, Vol. 2, 8th Edition, p. 121.

Table 3. Hardness Characteristics of Selected AISI 1031 Specimens After Heat Treatment

Specimen No.	Polished Surface Hardness (1) Average HR15N	Characteristics of Case Adjacent To Polished Surface (2) HR15N Range to Depth of 0.004 inch
1031-2 (3)	79.5	83 - 80.5
1031-3 (3)	73	79.5 - 76
1031-7	74 - 75.5	80.5 - 75
1031-8	71.5	78 - 76.5
1031-9	86	85 - 86
1031-11	68	91 - 90 R15T
1031-15	68	78.5 - 74

(1) 77-80 HR15N required.

(2) 77-80 HR15N required to depth of 0.004 inch, minimum.

(3) Hardened at manufacturer's laboratory.

Table 4. Hardness Characteristics of Selected AISI 1045 Specimens After Heat Treatment

Specimen No.	Polished Surface Hardness (1) Average HR30N	Characteristics of Case Adjacent To Polished Surface (2) HR30N Range to Depth of 0.004 inc
1045-2 (3)	75.5	75.5 - 75
1045-3 (3)	76	74
1045-7	60	67 - 72
1045-8	69.5	75 - 71.5
1045-12	75	74.5 - 73
1045-14	76	75 - 73.5
1045-15	75.5	75 - 74

(1) 80 HR30N required.

(2) 80 HR30N required to depth of 0.004 inch, minimum. Material to be through hardened.

(3) Hardened at manufacturer's laboratory.

Table 5. Hardness Characteristics of Selected W2 Specimens After Heat Treatment

cimen No.	Polished Surface Hardness (1) Average HR30N	Characteristics of Case Adjacent To Polished Surface (2) HR30N Range to Depth of 0.004 inch
2 (3)	75	64.5 - 66
3 (3)	74.5	74
5	87	71.5 - 71
6	78	66.5 - 68.5

80 HR30N required.

80 HR30N required to depth of 0.004 inch, minimum.

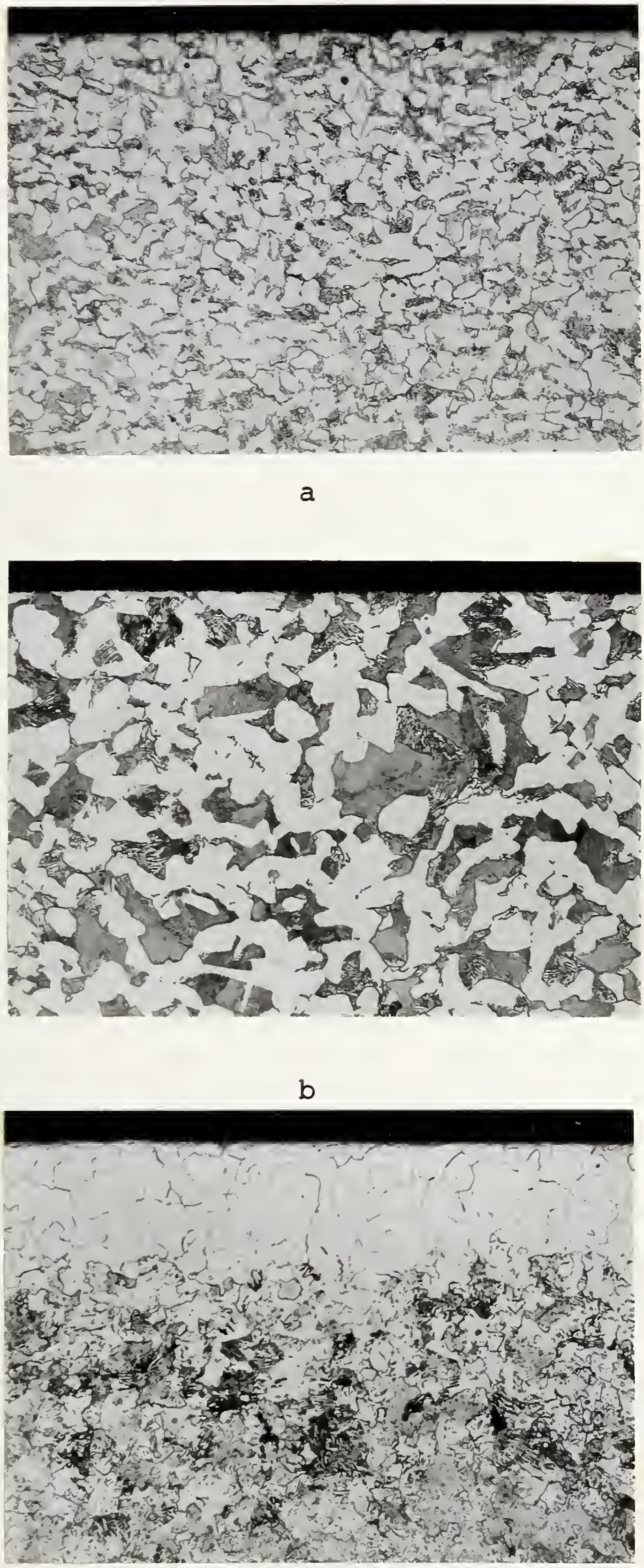
Hardened at manufacturer's laboratory.

Figure 1. Microstructures in Transfer Process Test Material Specimens, as-received. Etched with 4 percent nital. X 200

1a. Specimen 1031-1. Partially spheroidized carbides in a ferrite (white) matrix. ASTM grain size, 8-9. No decarburization is present adjacent to polished surface.

1b. Specimen 1045-1. Lamellar pearlite (dark) in a ferrite (white) matrix. ASTM grain size, 7. No decarburization is present adjacent to polished surface.

1c. Specimen W2-1. Decarburized zone (white ferrite grains) adjacent to polished surface. Mixture of lamellar pearlite and ferrite in transitional zone between decarburized zone and core. Core structure consists of pearlite and ferrite.



a

b

c

Figure 1.

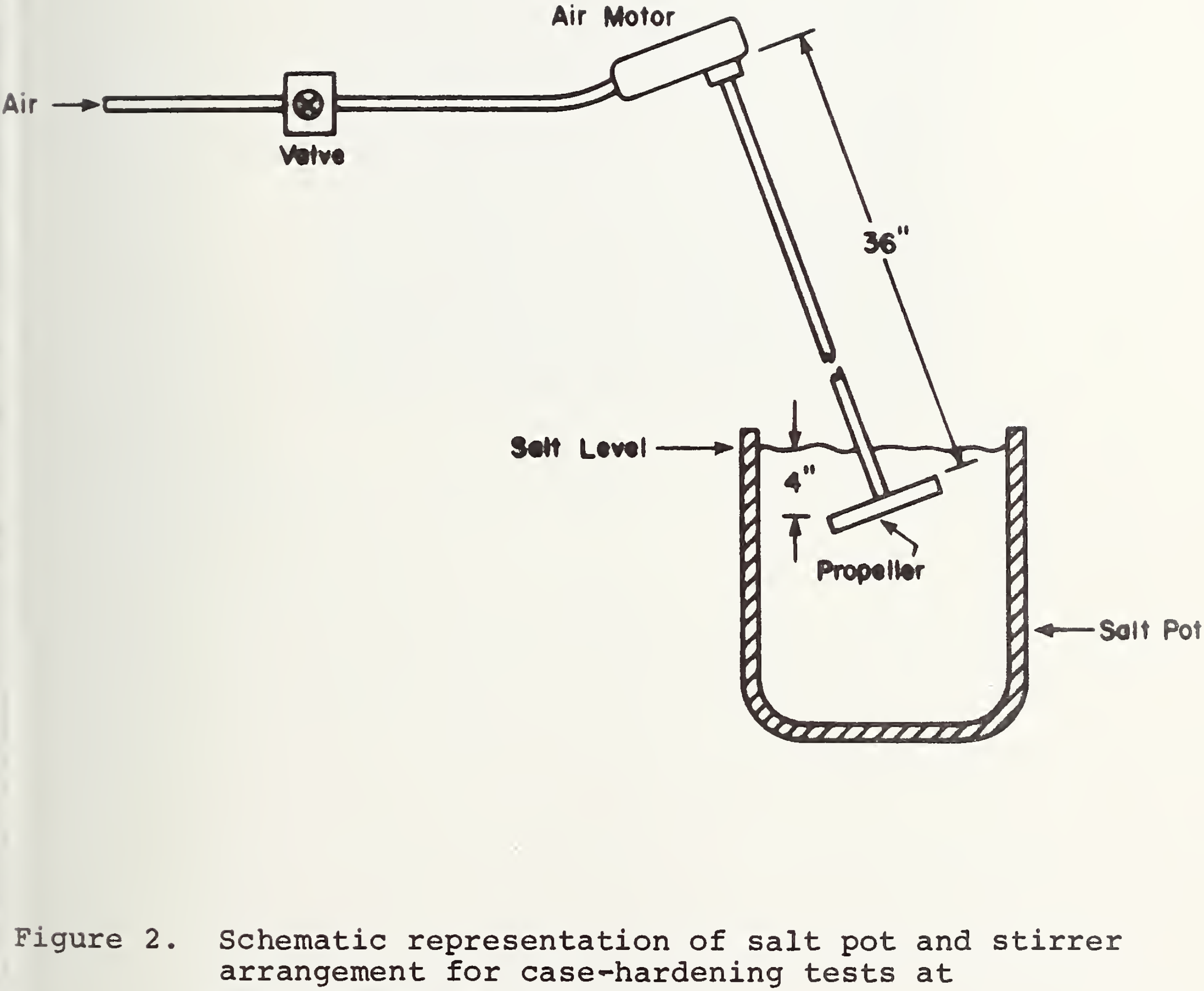


Figure 2. Schematic representation of salt pot and stirrer arrangement for case-hardening tests at manufacturer's laboratory.

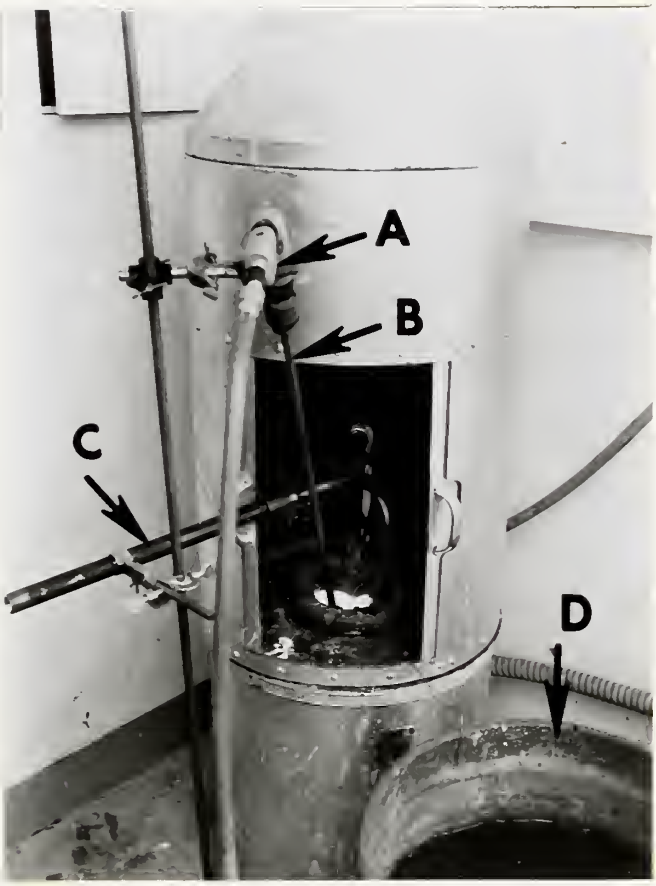


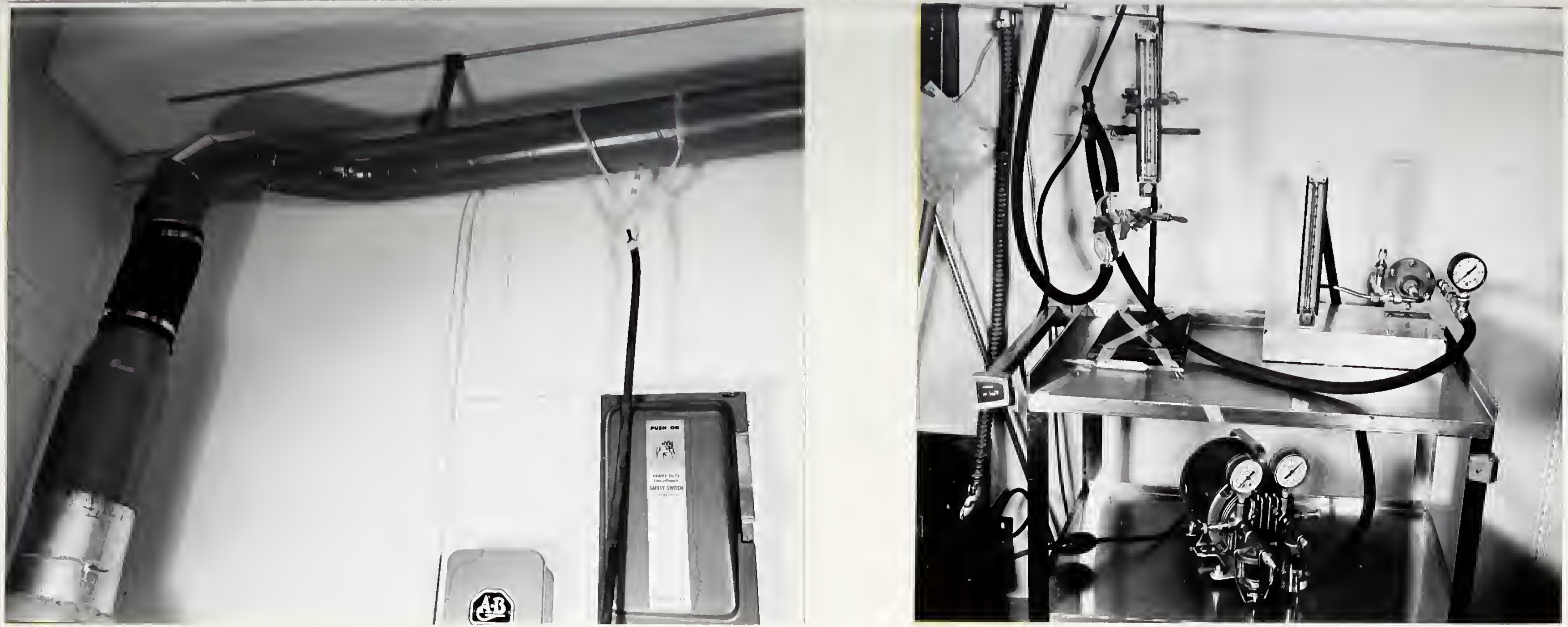
Figure 3. Salt pot arrangement for experimental case-hardening tests at NBS.

a. Air motor

b. Stirrer drive shaft

c. Conduit for auxiliary thermocouple lead wires

d. Quench tank



a

b

Figure 4. Equipment arrangement for exhaust air analysis.

a. Shows location of tap in exhaust air duct

b. Shows vacuum sampling apparatus

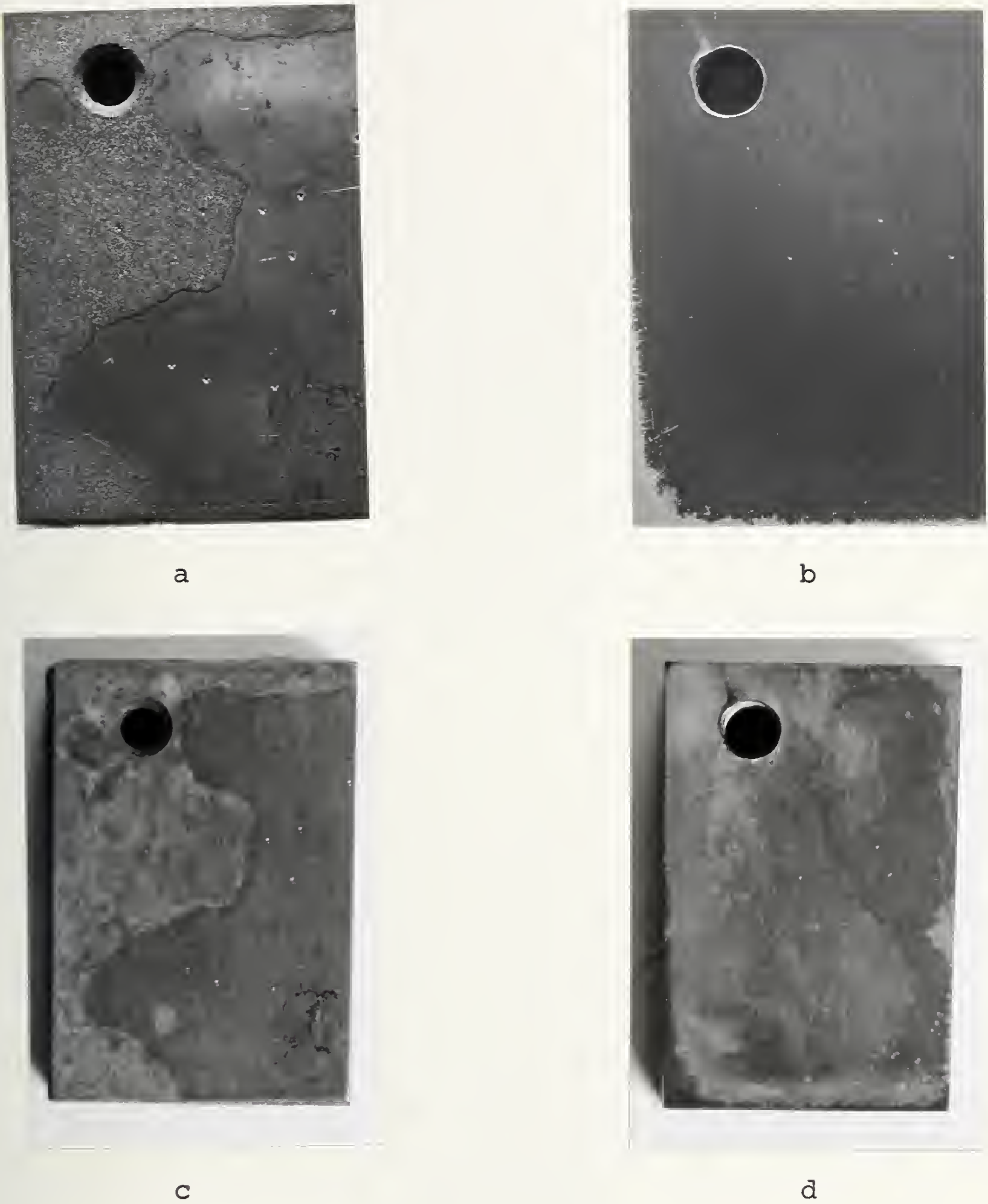


Figure 5. Appearance of polished surfaces of hardened specimens.

a. Coating on specimen 1031-14 before cleaning
b. Coating on specimen 1045-12 before cleaning
c. 1031-14 after cleaning
d. 1045-12 after cleaning

Figures 6 through 23

Microstructure and Properties of selected AISI 1031, AISI 1045 and W-2 Specimens.

Structures and hardness properties obtained from specific treatments and salt bath conditions are described.

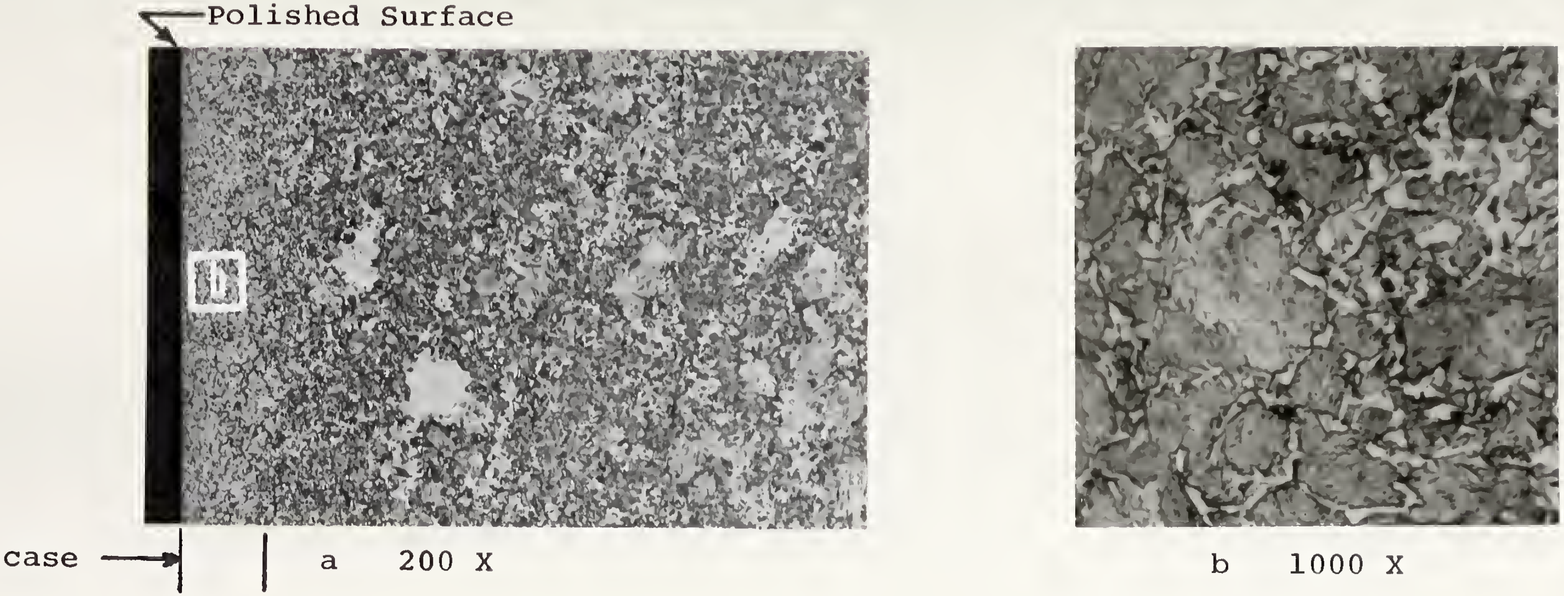
Each figure shows microstructures revealed by a four percent picral etchant:

a. Case and core microstructure at 200 X

b. Microstructure of case (insert area in a) at 1000 X

Figure 6. Specimen 1031-2

Austenitized at 1550F 36 minutes, oil quenched, double tempered 90 minutes at 400F. Specimen hardened at manufacturer's laboratory. No salt replenishment.



Case: Essentially tempered martensite with some grain boundary ferrite (white).

Core: Ferrite (white) in a matrix of tempered martensite (dark) large white areas are unresolved martensite.

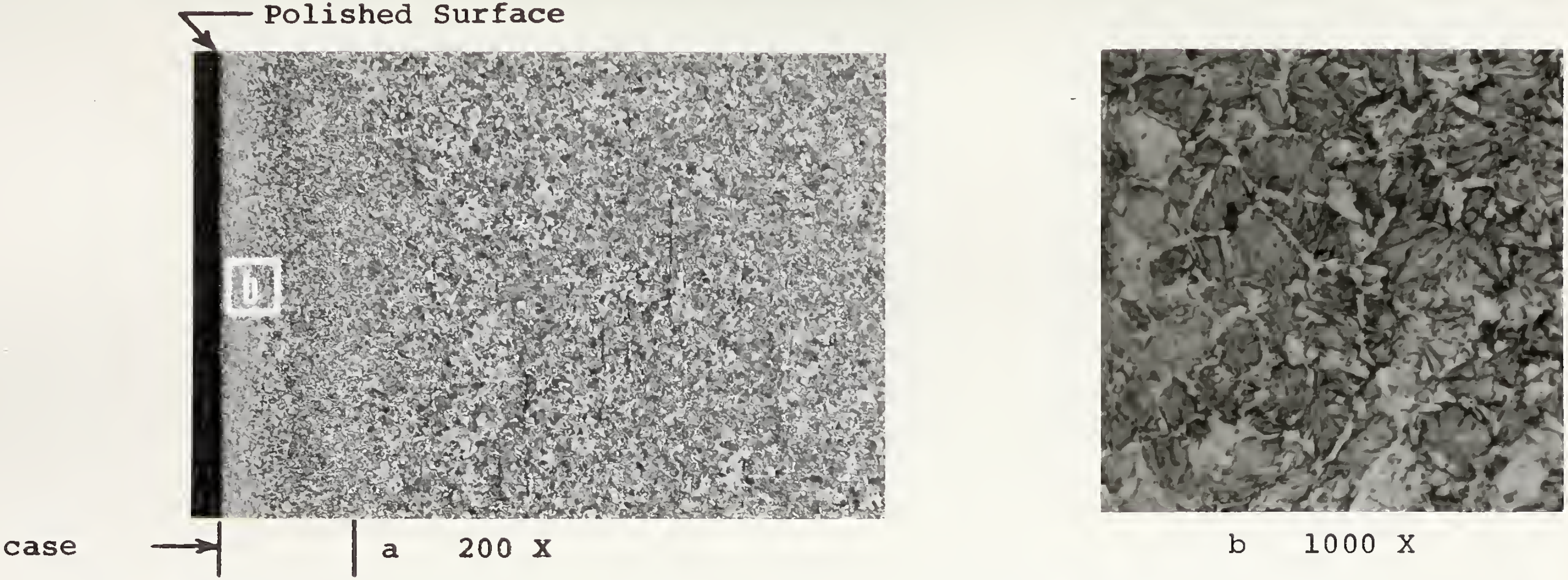
Case depth, from metallographic observation: approximately 0.0025 inch

Case depth, from hardness traverse: 0.006 inch

Hardness: 79.5 HR15N on polished surface. Range in case, 79.5 - 83 HR15N

Figure 7. Specimen 1031-3

Austenitized at 1550F 45 minutes, oil quenched, double tempered 90 minutes at 400F. Hardening time extended to determine effect on case depth. Hardened at manufacturer's laboratory. No salt replenishment.



Case: Predominantly tempered martensite with ferrite (white) in grain boundaries. Light area adjacent to polished surface is probably due to a carbonitriding effect.

Core: Essentially tempered martensite with ferrite (white) in grain boundaries. Large white areas are unresolved martensite.

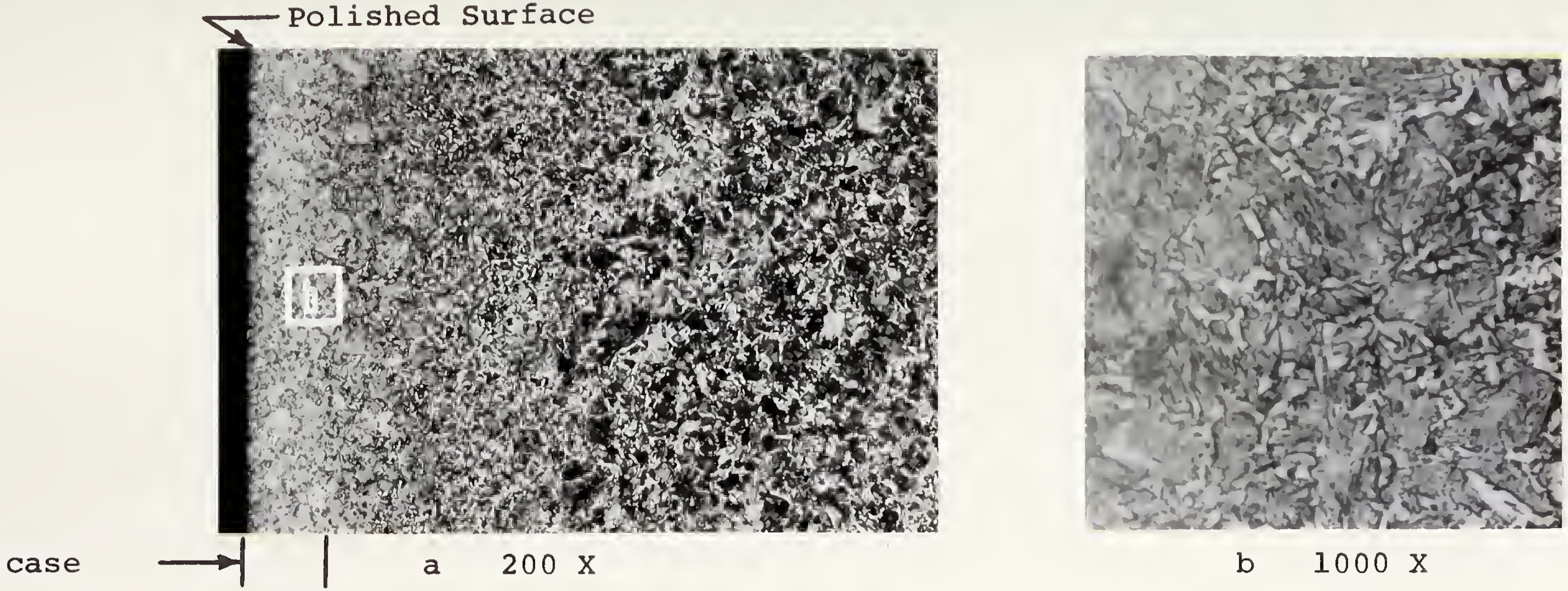
Case depth, from metallographic observation: approximately 0.0035 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 79.5 HR15N on polished surface. Range in case, 76 - 79.5 HR15N.

Figure 8. Specimen 1031-7

Austenitized at 1550F 40 minutes; oil quenched; double tempered 75 minutes at 450F, 75 minutes at 425F. Hardened at NBS. Fresh salt bath.



a 200 X

b 1000 X

Case: Essentially tempered martensite (dark) with ferrite (white) in grain boundaries. Ferrite grain boundary network is prominent in transition zone.

Core: Tempered martensite with ferrite in grain boundaries.

Case depth, from metallographic observation: approximately 0.002 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 74 - 75.5 HR15N on polished surface. Range in case, 70 - 80.5 HR15N

Figure 9. Specimen 1031-8

Austenitized at 1575F 40 minutes; oil quenched; double tempered, 75 minutes at 400F, 75 minutes at 375F. Hardened at NBS. LOCY additive and LOCYN pellets added to salt bath in replenishment.

a 200 X

b 1000 X

Case: Essentially tempered martensite with ferrite (white) in grain boundaries. Ferrite grain boundary network is prominant in transition zone.

Core: Tempered martensite with ferrite in grain boundaries.

Case depth, from metallographic observation: Approximately 0.002 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 71.5 HR15N on polished surface. Range in case, 76.5 - 78 HR15N.

Figure 10. Specimen 1031-9

Austenitized at 1585F 36 minutes; brine quenched; double tempered, 75 minutes at 450F, 75 minutes at 425F. Hardened at NBS. No salt replenishment.

a 200 X

b 1000 X

Case: Essentially tempered martensite.

Core: Tempered martensite.

Case depth, from metallographic observation: Approximately 0.0035 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 86 HR15N on polished surface. Range in case, 85 - 86.5 HR15N.

Figure 11. Specimen 1031-11

Austenitized at 1550F 36 minutes; oil quenched; double tempered, 75 minutes at 450F, 75 minutes at 425F. Hardened at NBS. Fresh salt bath.

a 200 X

b 1000 X

Case: Tempered martensite (dark) and ferrite (light).

Core: Tempered martensite and ferrite.

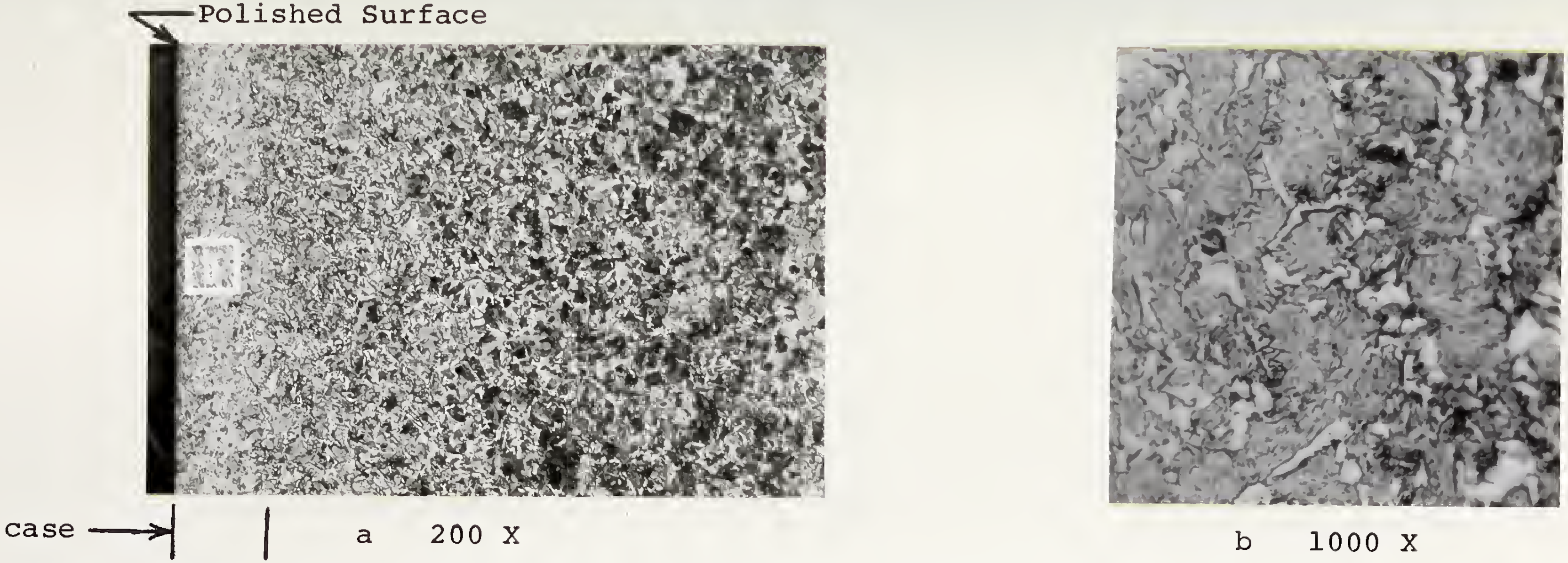
Case depth, from metallographic observation: Approximately 0.003 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 68 HR15N on polished surface. Range in case, 90 - 91 HR15T.

Figure 12. Specimen 1031-15

Austenitized at 1550F 36 minutes; oil quenched; double tempered, 75 minutes at 450F, 75 minutes at 425F. Hardened at NBS. LOCYN pellets added to salt bath for replenishment.



a 200 X

b 1000 X

Case: Tempered martensite (dark) and ferrite (white) in grain boundaries.

Core: Tempered martensite and grain boundary ferrite.

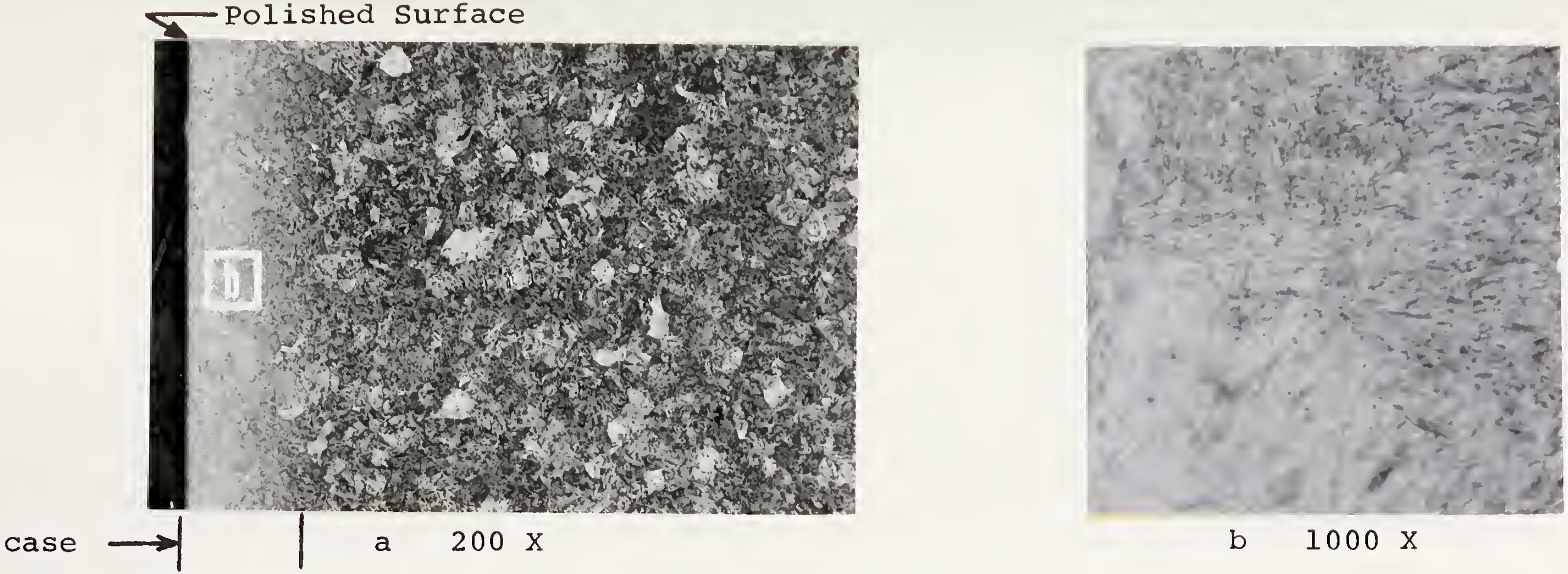
Case depth, from metallographic observation: Approximately 0.003 inch.

Case depth, from hardness traverse: 0.003 inch.

Hardness: 68 HR15N on polished surface. Range in case, 78 - 78.5 HR15N.

Figure 13. Specimen 1045-2

Austenitized at 1500F 30 minutes; brine quenched; tempered 90 minutes at 400F. Hardened at manufacturer's laboratory. Fresh salt bath.



a 200 X

b 1000 X

Case: Essentially tempered martensite.

Core: Tempered martensite.

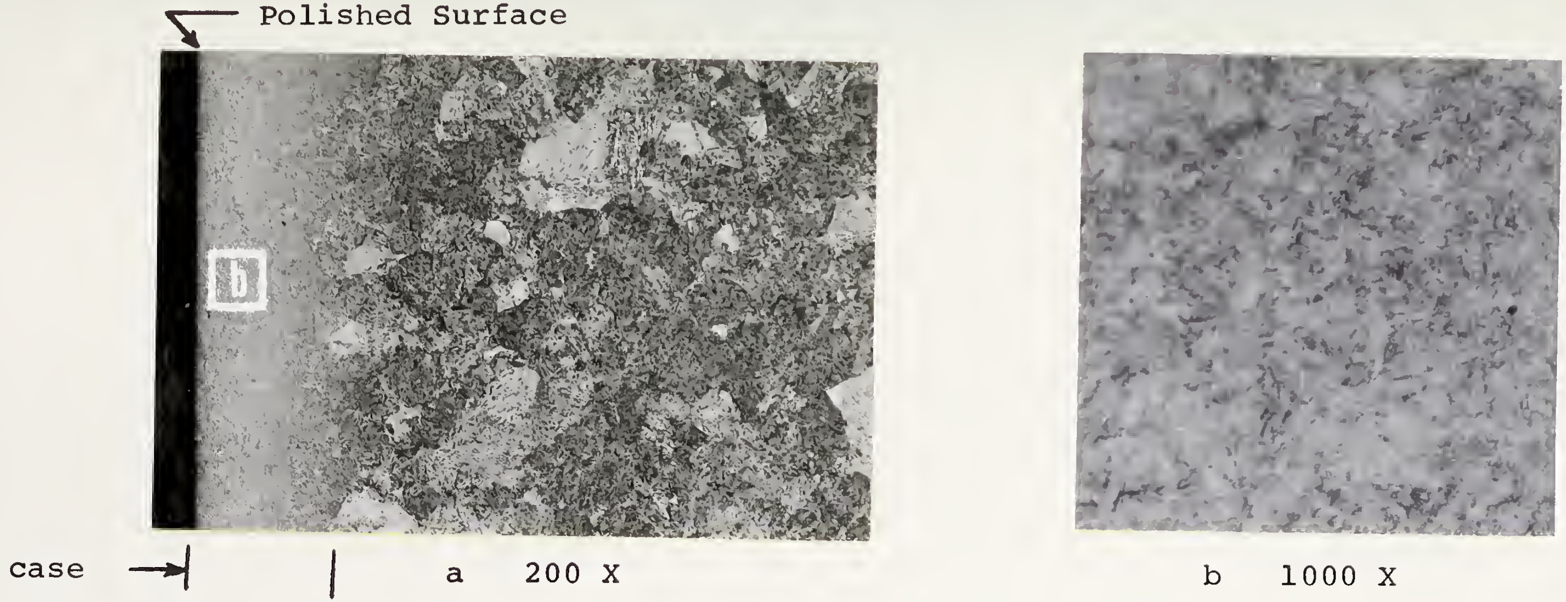
Case depth, from metallographic observation: Approximately 0.003 inch.

Case depth, from hardness traverse: 0.003 inch.

Hardness: 75.5 HR30N on polished surface. Range in case, 75 - 75.5 HR30N.

Figure 14. Specimen 1045-3

Austenitized at 1500F 45 minutes; brine quenched; tempered 90 minutes at 400F. Hardened at manufacturer's laboratory. LOCYN pellets added to salt bath for replenishment.



a 200 X

b 1000 X

Case: Tempered martensite.

Core: Tempered martensite.

Case depth, from metallographic observation: Approximately 0.0035 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 76 HR30N on polished surface. Case hardness, 74 HR30N.

Figure 15. Specimen 1045-7

Austenitized at 1480F 30 minutes; brine quenched; tempered 90 minutes at 400F. Hardened at NBS. NOCY additive and LOCYN pellets added to salt bath for replenishment.

a 200 X

b 1000 X

Case: Essentially tempered martensite.

Core: Tempered martensite with troostite (dark) in grain boundaries.

Case depth, from metallographic observation: Approximately 0.003 inch.

Case depth, from hardness traverse: 0.003 inch.

Hardness: 60 HR30N on polished surface. Range in case, 74 - 74.5 HR30N.

Figure 16. Specimen 1045-8

Austenitized at 1500F 30 minutes; brine quenched; tempered 75 minutes at 400F. Hardened at NBS. NOCY additive and LOCYN pellets added to salt bath for replenishment.

a 200 X

b 1000 X

Case: Essentially tempered martensite.

Core: Essentially tempered martensite.

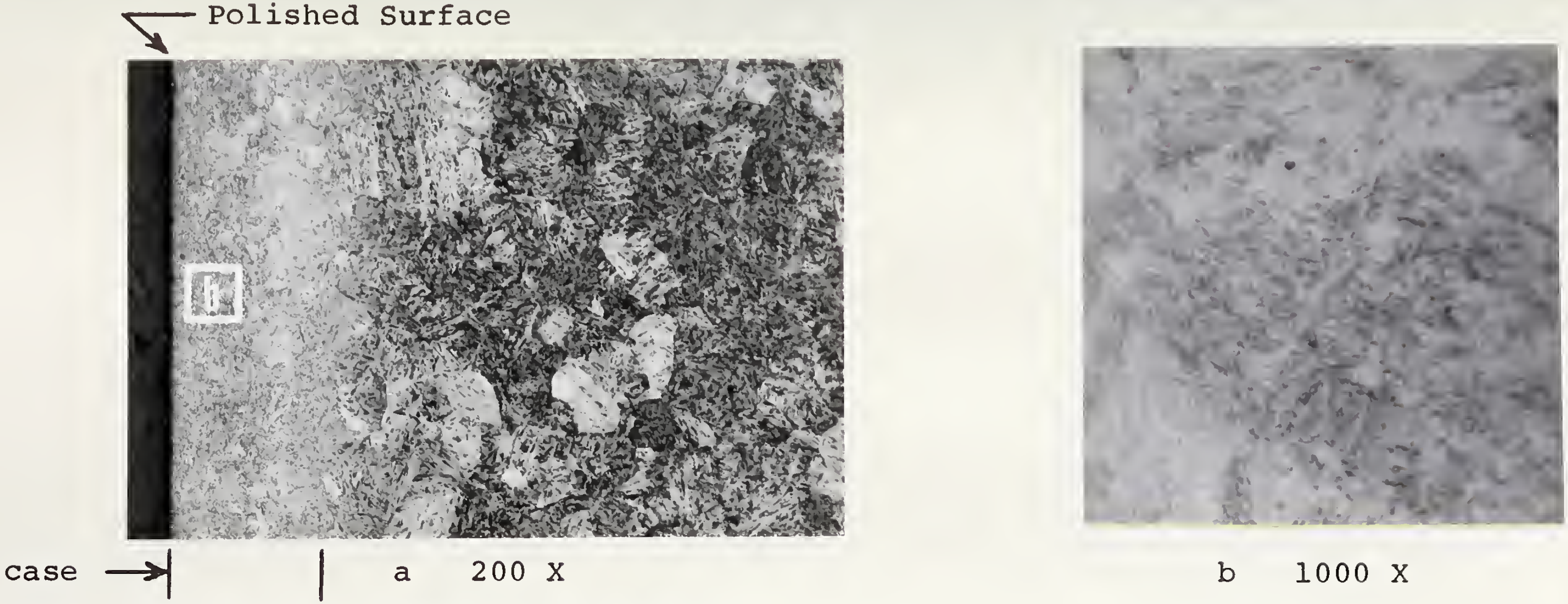
Case depth, from metallographic observation: Approximately 0.003 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 69.5 HR30N on polished surface. Range in case, 72 - 75 HR30N.

Figure 17. Specimen 1045-12

Austenitized at 1480F 30 minutes; brine quenched; tempered 90 minutes at 400 F. Hardened at NBS. LOCYN pellets added to salt bath for replenishment.



a 200 X

b 1000 X

Case: Essentially tempered martensite.

Core: Martensite.

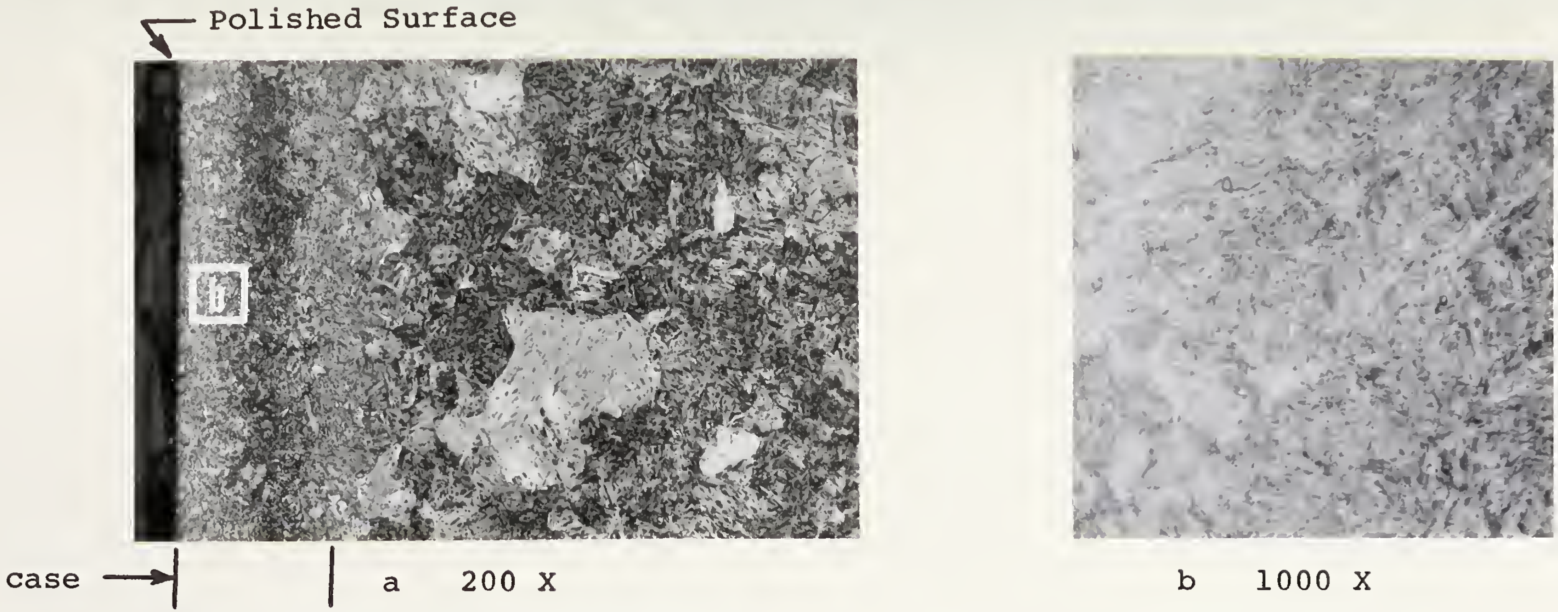
Case depth, from metallographic observation: Approximately 0.004 inch.

Case depth, from hardness traverse: 0.0045 inch.

Hardness: 75 HR30N on polished surface. Range in case, 73 - 74.5 HR30N.

Figure 18. Specimen 1045-14

Austenitized at 1480F 30 minutes; brine quenched; tempered 90 minutes at 400F. Hardened at NBS. LOCYN pellets added to salt bath for replenishment.



a 200 X

b 1000 X

Case: Essentially tempered martensite.

Core: Martensite

Case depth, from metallographic observation: Approximately 0.004 inch.

Case depth, from hardness traverse: 0.004 inch.

Hardness: 76 HR30N on polished surface. Range in case, 73 - 74.5 HR30N.

Figure 19. Specimen 1045-15

Austenitized at 1480F 30 minutes; brine quenched; tempered 90 minutes at 400F. Hardened at NBS. LOCYN pellets added to salt bath for replenishment.

a 200 X

b 1000 X

Case: Essentially tempered martensite.

Core: Martensite.

Case depth, from metallographic observation: Approximately 0.004 inch.

Case depth, from hardness traverse: 0.0045 inch.

Hardness: 75.5 HR30N on polished surface. Range in case, 74 - 75 HR30N.

Figure 20. Specimen W2-2

Austenitized at 1550F 60 minutes; brine quenched; tempered 90 minutes at 400F. Hardened at manufacturer's laboratory. No salt replenishment.

a 200 X

b 1000 X

Case: Carbides (dark) in a ferrite matrix (light).

Core: Essentially tempered martensite.

Case depth, from metallographic observation: Approximately 0.003 inch.

Case depth, from hardness traverse: 0.006 inch.

Hardness: 75 HR30N on polished surface. Range in case, 64.5 - 66 HR30N.

Figure 21. Specimen W2-3

Austenitized at 1500F 60 minutes; brine quenched; tempered 90 minutes at 400F. Hardened at manufacturer's laboratory. LOCYN pellets added to salt bath for replenishment.

a 200 X

b 1000 X

Case: Carbides (dark) in a ferrite matrix (light).

Core: Essentially tempered martensite.

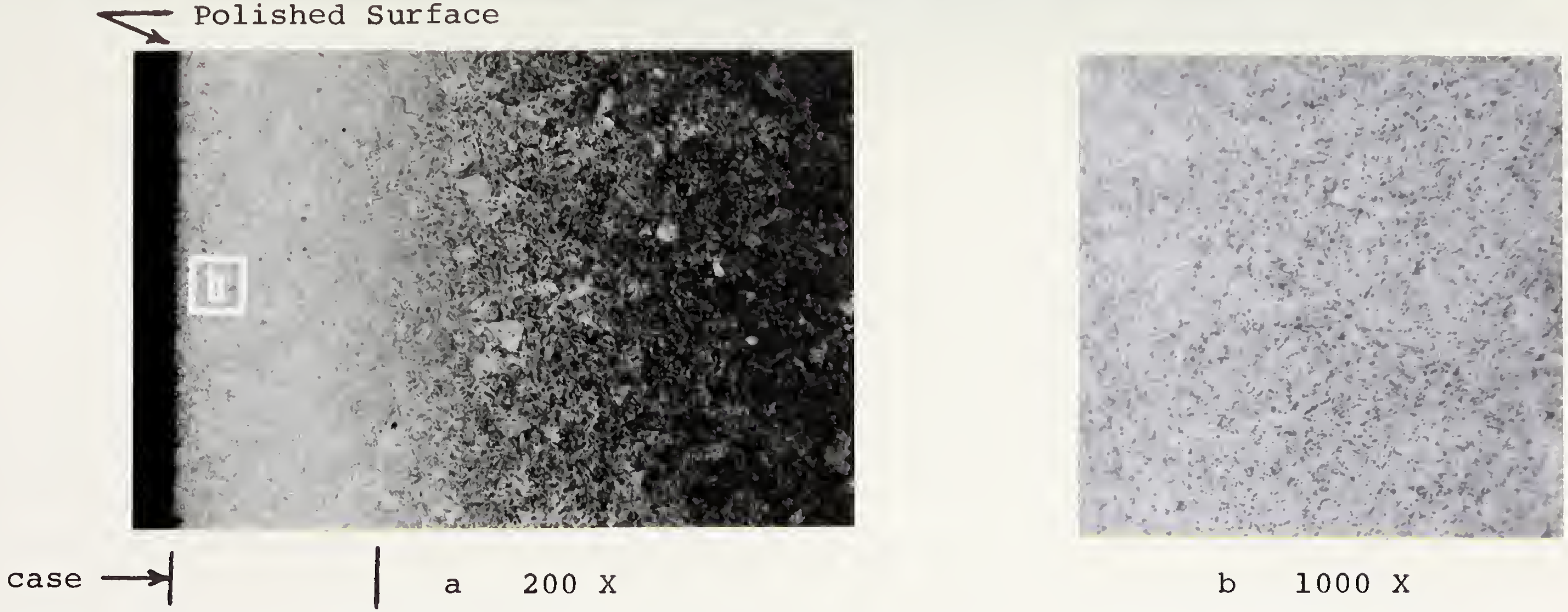
Case depth, from metallographic observation: Approximately 0.004 inch.

Case depth, from hardness traverse: 0.006 inch.

Hardness: 74.5 HR30N on polished surface and to a depth of 0.006 inch from polished surface.

Figure 22. Specimen W2-5

Austenitized at 1550F 60 minutes; brine quenched; tempered 90 minutes at 375F. Hardened at NBS. NOCY additive and LOCYN pellets added to salt bath for replenishment.



Case: Carbides (dark) in a ferrite matrix (light).

Core: Essentially tempered martensite.

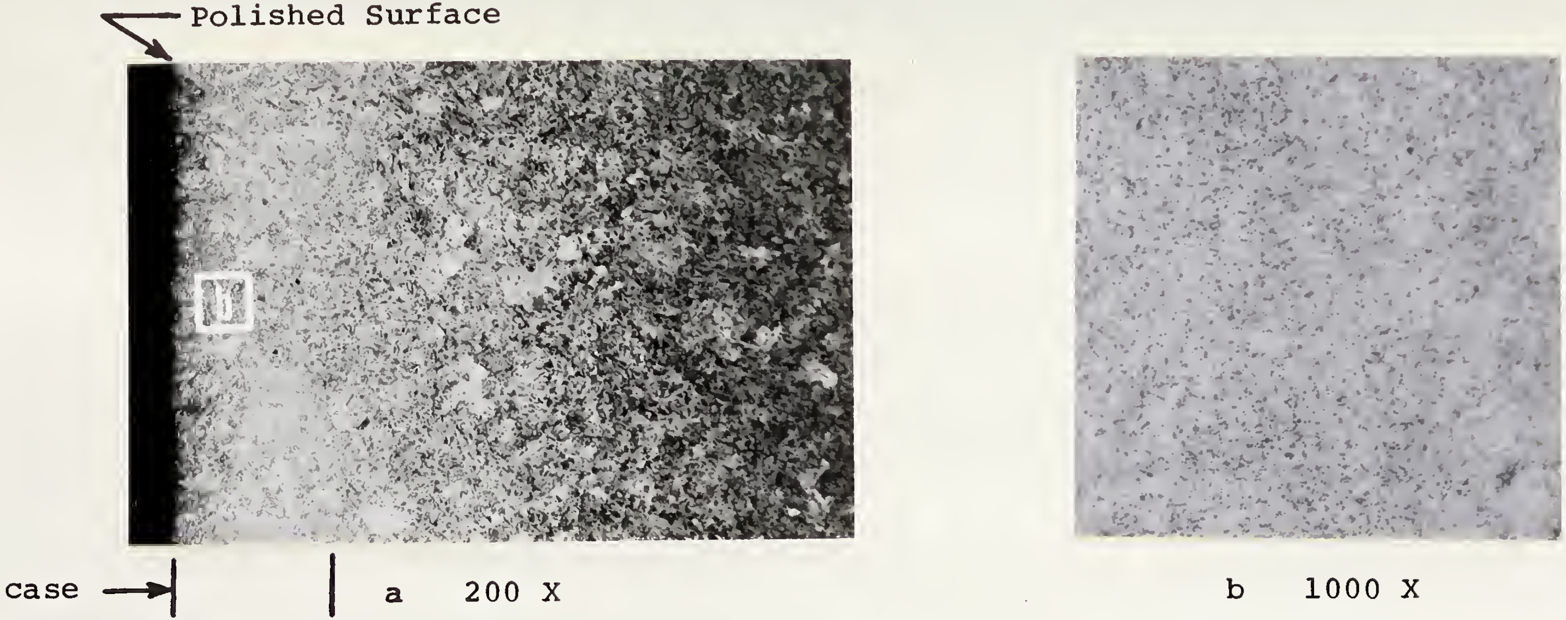
Case depth, from metallographic observation: Approximately 0.006 inch.

Case depth, from hardness traverse: 0.006 inch.

Hardness: 87 HR30N on polished surface. Range 70 - 71.5 HR30N to a depth of 0.006 inch, from polished surface.

Figure 23. Specimen W2-6

Austenitized at 1575F 60 minutes; brine quenched; tempered 75 minutes at 375F. Hardened at NBS. NOCY additive and LOCYN pellets added to salt bath for replenishment.



a 200 X

b 1000 X

Case: Carbides (dark) in a ferrite matrix (light).

Core: Essentially tempered martensite.

Case depth, from metallographic observation: Approximately 0.005 inch.

Case depth, from hardness traverse: 0.006 inch.

Hardness: 78 HR30N on polished surface. Range 66.5 - 72 HR30N to a depth of 0.006 inch from polished surface.

APPENDIX

ORM **NBS-348**
(12-65)

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

REPORT OF ANALYSIS

Requested by I. J. Feinberg

Div. Req. No. 5125 Project No. 3120541

Section 312.01

The work performed is described in Analytical Report "The Sampling and Analysis for Cyanide in the Exhaust Air from a Steel-Hardening Process." A copy of which is attached.

John K. Tay

John K. Taylor
Chief
Air and Water Pollution
Analysis Section
Analytical Chemistry Division

J. I. Shultz

James I. Shultz
Service Analysis Coordinator
Analytical Chemistry Division

November 15, 1974

75-43

ANALYTICAL REPORT

The Sampling and Analysis for Cyanide in the Exhaust Air from a Steel-Hardening Process

Barry C. Cadoff and John K. Taylor
Air Pollution Analysis Section
Analytical Chemistry Division

Requested by

Irving J. Feinberg
Mechanical Properties Section
Metallurgy Division

The Sampling and Analysis for Cyanide in the Exhaust Air from a Steel-Hardening Process

This report describes the collection and analysis for cyanide of air samples taken from the exhaust air of a steel-hardening process. The sample collection was performed on October 3, 1974.

Sampling Procedure and Equipment

The steel-hardening process under investigation involves the use of a proprietary molten salt mixture, contained in a salt pot, in which is immersed the steel item that is to be hardened. Positioned above the salt pot is an exhaust hood and duct that vents gases or particulates produced during the process.

Air samples were collected by inserting a sampling tube into a hole drilled in the duct. The sampling tubes contained 4 g of Ascarite, 20-30 mesh, a formulation consisting of sodium hydroxide on asbestos. This material traps acidic gases including any HCN which might be formed during the process. The sampling tube was connected to a vacuum sampling system capable of maintaining a constant flow rate. (This system has been described in NBSIR 74-527, "Development of Solid State Samplers for Work Atmospheres", B. Greifer, B. C. Cadoff, J. Wing and J. K. Taylor", June 1974.) The flow was adjusted to 1.0 liter/min using a calibrated rotameter. The sampling times were measured with a stopwatch.

Sample Collection

The use of a high-capacity sampling tube and a constant-flow sampling system made it feasible to use a single sampling tube for periods of one or more hours, without having to periodically check the flow rate. A total of four sampling tubes were used to monitor the steel-hardening process. Descriptions of the process are presented along with data on the duration of sampling.

Air Sample #1

The salt pot was charged with the commercial product No-Cy Base Salt and the heating was begun at 8:45 A.M. Sampling was started at 9:45 A.M. when the pot temperature had reached 500°F. At 11:10 the salt bath was molten and more No-Cy Base Salt was added. Stirring of the salt bath was begun at 11:30 A.M Sampling was stopped at 11:46 A.M.

Total sampling time: 121 min., 10 sec.

Air Sample #2

Sampling was started at 12:13 P.M. (temp. 1550°F) at which time the No-Cy Additive (black powdery material) was added. Sampling was stopped at 12:28 P.M.

Total sampling time: 15 min.

Air Sample #3

Sampling was begun at 12:30 P.M., at which time the Lo-Cy N Pellets were added. At 1:35 P.M. two steel samples designated 1031-15 and 1031-16 were placed in the molten salt to test its steel-hardening characteristics. Air sampling was stopped at 1:51 P.M.

Total sampling time: 81 min., 5 sec.

Air Sample #4

Sampling was started at 1:54 P.M. Steel samples 1031-15 and 1031-16 were removed from the salt pot at 2:15 P.M. and quenched in a bath containing 2500 ml distilled water. At 2:24 P.M. steel samples 1031-17 and 1031-18 were dipped in the salt pot and were removed at 3:04 P.M. and quenched in the water bath. Air sampling was stopped at 3:30 P.M.

Total sampling time: 96 min., 10 sec.

Water Sample "B"

A sample of the quenching water, Water Sample "B", was taken after the four steel samples had been quenched.

Water Sample "A"

Before any of the steel samples had been quenched, a sample of the quenching water was taken and labeled, Water Sample "A".

Analysis and Results

To analyze for cyanide, the cyanide ion-selective electrode was used. For the calibration of this procedure a series of standard cyanide solutions, covering the range from 10^{-5} to 10^{-3} M were prepared. The contents of each sampling tube was extracted with hot water, filtered and diluted to exactly 100 ml. The ion-selective electrode was then used to determine the quantity of cyanide. A blank sampling tube was also analyzed.

Water samples "A" and "B" were prepared for analysis by adding 15 ml of the water sample to 15 ml of 1 M NaOH. The analytical technique for cyanide in the water samples was the same as for the air samples.

No cyanide was found in air samples #1, 2 and 4 and Water Sample "A". Air Sample #3 gave a solution containing 5.5×10^{-6} cyanide. This is equivalent to a concentration in the sampled air of 0.18 µg/1 (0.17 ppm) cyanide. Water Sample "B" gave a solution containing 2.6×10^{-5} M cyanide which is equivalent to a total of 3.4 mg cyanide in the 2500 ml quenching water.

Other Observations

The ingredients that comprise the steel-hardening formulation were briefly examined.

No-Cy Base Salt

Two g of No-Cy Base Salt was dissolved in 50 ml water, to give a solution with a pH = 12.4. This solution did not contain cyanide.

No-Cy Additive

One g of No-Cy Additive was added to a beaker containing 50 ml water. A black powdery material floated to the top of the water and a white crystalline material sank to the bottom of the beaker. The white material dissolved upon heating. Solution contained no cyanide and had pH = 11.3.

Lo-Cy N Pellets

One pellet (1.80 g) was dissolved in 50 ml water, ph = 11.9 Fifteen ml of this solution was added to 15 ml of 1 M NaOH and this solution contained 2.7 x 10^{-5} M cyanide. This is equivalent to 0.004 percent cyanide, by weight, in the pellet.

Conclusions

Throughout most of the steel-hardening process no cyanide is emitted into the exhaust air. In the case of air sample #3 a small amount of cyanide was found; this level of cyanide, 0.17 ppm (averaged over the entire sampling period) is less than 2 percent of the OSHA permissible concentration level for HCN in an eight hour working day. Most likely the cyanide is not in the gaseous HCN form, since the salt mixture is strongly basic and HCN would not be expected to be formed, but rather the cyanide may be in the particulate state and may have been formed and emitted during the addition of the Lo-Cy N pellets, at which time splattering was observed. This speculation is supported by the fact that a relatively large amount of cyanide was found in the quench water, due to transfer of some of the molten salt mixture to the water during quenching. The cyanide found in the Lo-Cy N Pellet, 0.004 percent by weight, can be considered as a trace contaminant.

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UPPLEMENTARY NOTES

BSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A new molten salt hardening process has been evaluated for hardening steels used the three stage transfer process for printing stamps. Evaluation of the new rocess was undertaken because virtually all cyanide salts are eliminated as ngredients in the process. It was found that complete elimination of cyanide missions is not achieved in the new process, however, the level of cyanide emitted oes meet OSHA requirements. A case-hardening capability was exhibited in experimental ests on Bureau of Engraving and Printing materials, but case depths and hardness did ot meet Bureau of Engraving and Printing requirements. Further development of the ew process is needed before it can be considered for the Bureau of Engraving and rinting.

KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Carburizing; case; cyanide; emissions; hardenability; nitriding; substitution; toxicity

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