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ALUMINUM-COPPER-NICKEL ALLOY AS A POSSIBLE SUBSTITUTE FOR ALPHA BRASS FOR USE IN CARTRIDGE CASES

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THESIS

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SUBJECT "Aluminum-Copper-Nickel Alloy as a Possible Substitute for Alpha Brass for Use in Cartridge Cases."

PRESENTED BY Eugene C. Rook, Lieutenant (jg), U.S.Navy.

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APPROVED BY THE FACULTY

DIRECTOR.

GENERAL OUTLINE

Aluminum-Copper-Nickel Alloy as a Possible Substitute for Alpha Brass for Use in Cartridge Cases.

I Introduction.

1. The present tendency toward reduction of armaments in general and reduction in size of men-of-war in particular keeps the Navy Department constantly on the lookout for improvements which will cause an increase in battle-worthiness of the vessels it is allowed. In former times the general policy was to first decide on armor, armament, and speed of the vessel and then design a hull capable of carrying the load. At the present time, with tonnages limited by treaty, the problem is exactly reversed. The size of the hull is fixed and then armor, armament, and speed balanced to fit. Consequently, any reduction in dead weight is highly desirable, and the outstanding opportunity for effecting this reduction is to substitute light metal alloys for the heavier metals and alloys in as many places as possible.

2 Certain types of Naval vessels employ fixed ammunition[1] exclusively while others employ it in certain groups of their guns. Those using fixed ammunition exclusively are the smaller vessels where a saving in weight of dead load means a material increase in battle-worthiness. As a further consideration, however, the reduction in weight of the unit charge is important when it is realized that with even the most modern mechanized loading apparatus the charge is manually handled at one or more points in the

ammunition supply chain.

The present work was undertaken with the hope of determining a light alloy which might be suitable for use in cartridge cases. A rough estimate places the possible reduction in weight of the unit charge at 15-30 percent.

3. In adapting a light alloy to such use many difficulties are encountered. The alloy must have the following properties: (1) low specific gravity; (2) melting point and thermal conductivity sufficiently high to enable it to withstand elevated temperatures for short intervals of time; (3) strength and hardness to enable it to withstand accidental knocks in handling and prevent its extrusion into the extractor recess during firing; (4) sufficient elasticity to cause it to spring at the instant of firing and allow the gun to take the load, subsequently returning to its initial form when the pressure is released; (5) ductility to allow deep drawing during manufacture. Physical properties of an alloy as usually determined will give only a good indication of how that alloy will act in a particular application. The present instance is not an exception to this statement and it is admittedly true that in this case they will give only a general indication. The only worthwhile test must be the actual use of the alloy for the particular purpose.

Light alloys have been tried for this purpose with no apparent success as yet.[2] That work is being continued with the assistance of the Aluminum Company of America's Engineer Sales Department but it is confined to adaptations of the standard commercial alloys.

4. From an inspection of the literature [3,4,5,6,7] the conclusion was reached that a suitable light alloy might be found in the Aluminum-Copper-Nickel system. It was previously known that alloys 2S[9] and 51S[10] had been tried. The alloy 2S (commercially pure aluminum) gave fair results but was far from a success due to its softness. The alloy 51S as used was practically a total failure. From this it might be considered that the melting point of the 2S was sufficiently high, and the melting point of the 51S was sufficiently low, due to alloying additions, to prevent or allow intergranular melting. A permissible assumption is that a light Aluminum-Copper-Nickel alloy with a melting point near that of the 2S and strength and hardness superior to that of the aluminum might be successful.

5. The alloys to be investigated were basically the 96Al-4Cu alloy with ½, 1, 2, and 4% nickel substituted for an equivalent amount of aluminum. The general plan of work consisted of

(1) Determining liquidus and solidus for each alloy.

(2) Determining effect of nickel content by

(a) Microstructure study

(b) Hardness tests

(3) Determining physical properties with various heat treatments.

6. It is desired at this point to make the following acknowledgements:

(1) To Commander W.E.Brown, U.S.Navy, for his initial suggestion and subsequent help.

(2) To Mr. E. H. Dix, Jr. of the Aluminum Company of America and his staff for furnishing the alloys and subsequent assistance and advice in the metallographic work and in making the tensile specimens.

(3) To Mr. G. P. Halliwell of the Carnegie Institute of Technology faculty for his advice and assistance.

II. Material, Apparatus, and Methods

7. The analyses of the four alloys used are shown in Plate 1. They were prepared and analyzed at the Research Laboratory, Aluminum Company of America, New Kensington, Pa. The base metal was the high purity grade of aluminum known as grade 7A.[11]

8. A small nichrome-wound resistance furnace was used for the study of effects of heat treatment. Temperature control was entirely by hand. The temperatures were determined by a noble-metal thermocouple which was calibrated against a secondary standard of known accuracy. The potentiometers used were (1) a Leeds and Northrup Type K for the solidus and liquidus determinations and (2) a Leeds and Northrup portable type, calibrated against the Type K, for temperature control of the furnace. A "drop-bottom" for the furnace was built which would permit a quenching interval of approximately 1/5 second. The temperature differences within the furnace at 600°C. at the level of the platform were 4°C. from side to center, 4°C. to a distance of 1-½" above the platform.

9. Procedure

(1) Using carbon crucibles and with the thermocouples immersed in the metal and protected from it by a silica tube cooling and heating curves were taken on each of the four alloys to determine their solidus and liquidus temperatures. At least two curves were taken on heating or cooling each alloy and in most cases three or more. The results, as tabulated in Plate 2, are believed to be accurate within 5°C.

(2) After determining the solidus and liquidus temperatures samples ½"x½"x1/8" of each alloy were cut. Taking them in groups of four (one of each alloy) they were placed in the furnace, which had been rigged with the drop-bottom, and given the following heat treatment: heated to a temperature of 590°C. and maintained at that temperature (± 5°C.) for ½ hour. The furnace was then allowed to cool slowly to various temperatures ranging from 247°C. to 540°C. and after holding at this temperature ½ hour the specimens were quenched. The necessity of this fast quenching is obvious. The resulting specimens were then polished and etched with 1% HF (swab, 8 sec.). They were studied to determine the amounts and nature of the inclusions. Four typical examples of the structures are shown in the accompanying micrographs (Plates 3-6).

(3) One group of specimens was then maintained at 618°C. for ½ hour and quenched. Upon polishing and etching with the 1% HF it was seen that incipient melting had commenced. This is shown in Plate 7 for alloy #2. Similar conditions were noted in the other three.

(4) Hardnesses (Rockwell B) were taken immediately upon quenching in an effort to determine the advent of any precipi-

tation. The results are plotted in Plate 8.

(5) A group of specimens were quenched after soaking for ½ hour at 590°C. and then aged at various temperatures ranging from 100°C. to 450°C. for an additional ½ hour. The aging at 100°C. was done in boiling water and at the higher temperatures in the nichrome-wound furnace. They were air cooled from the aging temperatures. Hardness (Rockwell E, 1/8" ball, 100 kg. load, B scale) was taken after aging and the results plotted as shown in Plate 9.

(6) The #1 and #4 half-inch plates were then rolled down, first hot and then finished with a 50% cold reduction. the final thickness was 0.064" (14 gage, A.W.G.). Flat tensile coupons were then punched and milled. A series of the test pieces were heat-treated as in (5) and physical properties determined for the two alloys in the cold-rolled and heat-treated conditions. At least two specimens were tested for each alloy and heat-treatment. The average results are plotted in plates 10-12 inclusive.

(7) The microstructure of alloys #1 and #4 after quenching and aging at 100°C. is shown in plates 13 and 14.

III Data and Results

10. Index of Plates

PLATE 1

Alloy	Si	Fe	Cu	Ni	Al (diff.)
#1	.04	.01	4.20	.56	95.19
#2	.02	.01	4.16	1.10	94.71
#3	.03	.02	4.00	2.00	93.95
#4	.03	.03	4.04	4.05	91.85

ANALYSES OF ALLOYS

PLATE 2

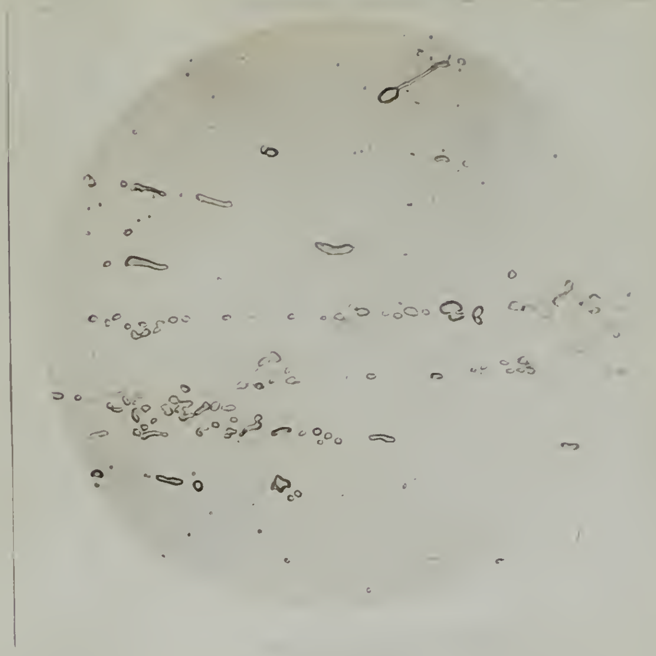
Alloy		#1	#2	#3	#4
Liquidus	Heating	648	646	637	635
	Cooling	645	641	640	636
Solidus	Heating	620	620	625	618
	Cooling	617	620	620	617

Degrees Centigrade

LIQUIDUS AND SOLIDUS DETERMINATIONS

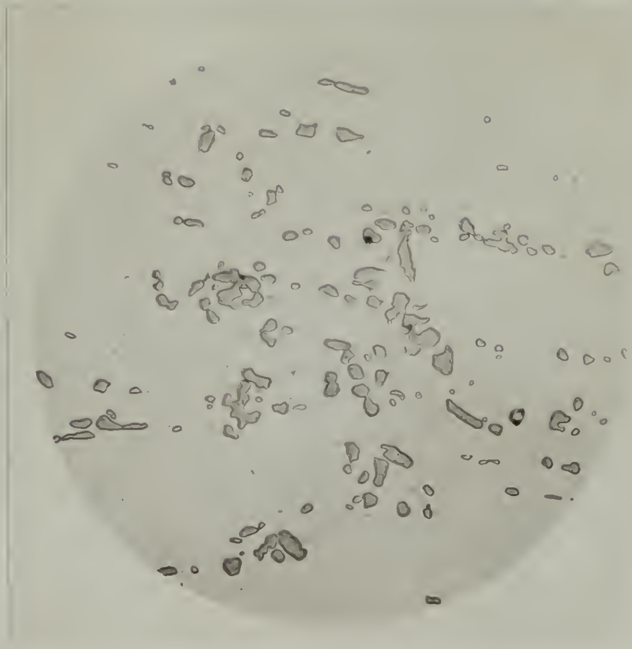
Alloy #1

Quenched from 590°C.
Unetched X500



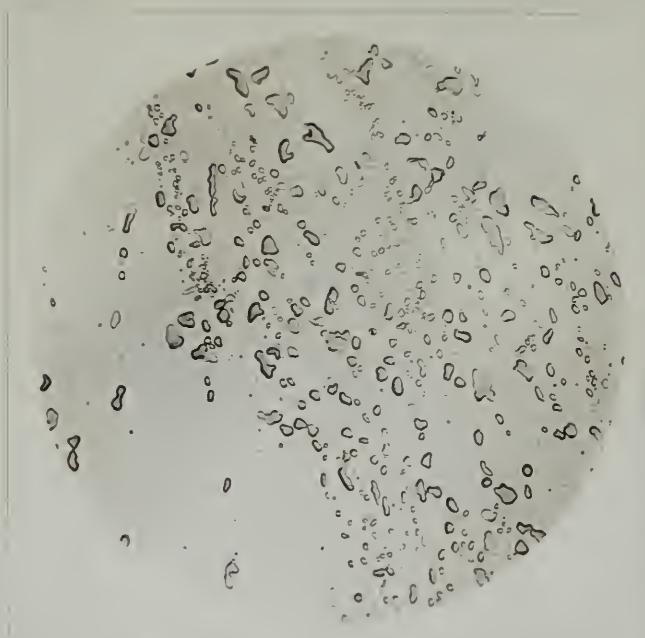
Alloy #2

Quenched from 590°C.
Unetched X500



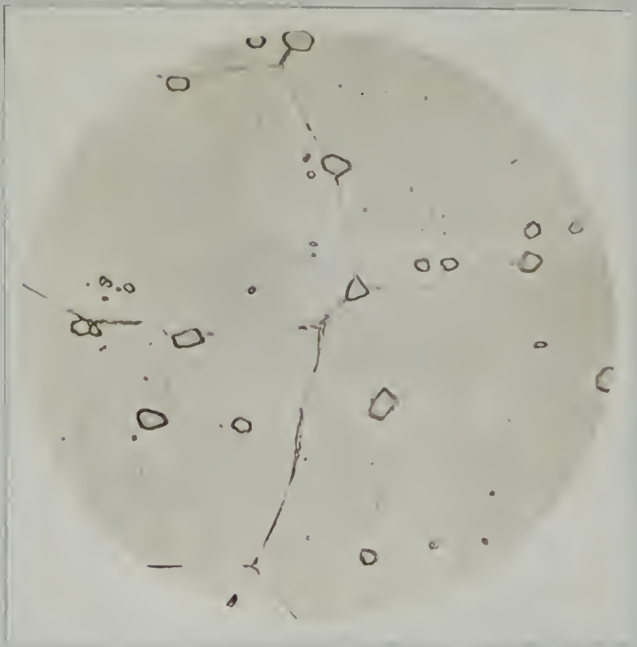
Alloy #3

Quenched from 590°C.
Unetched X500



Alloy #4

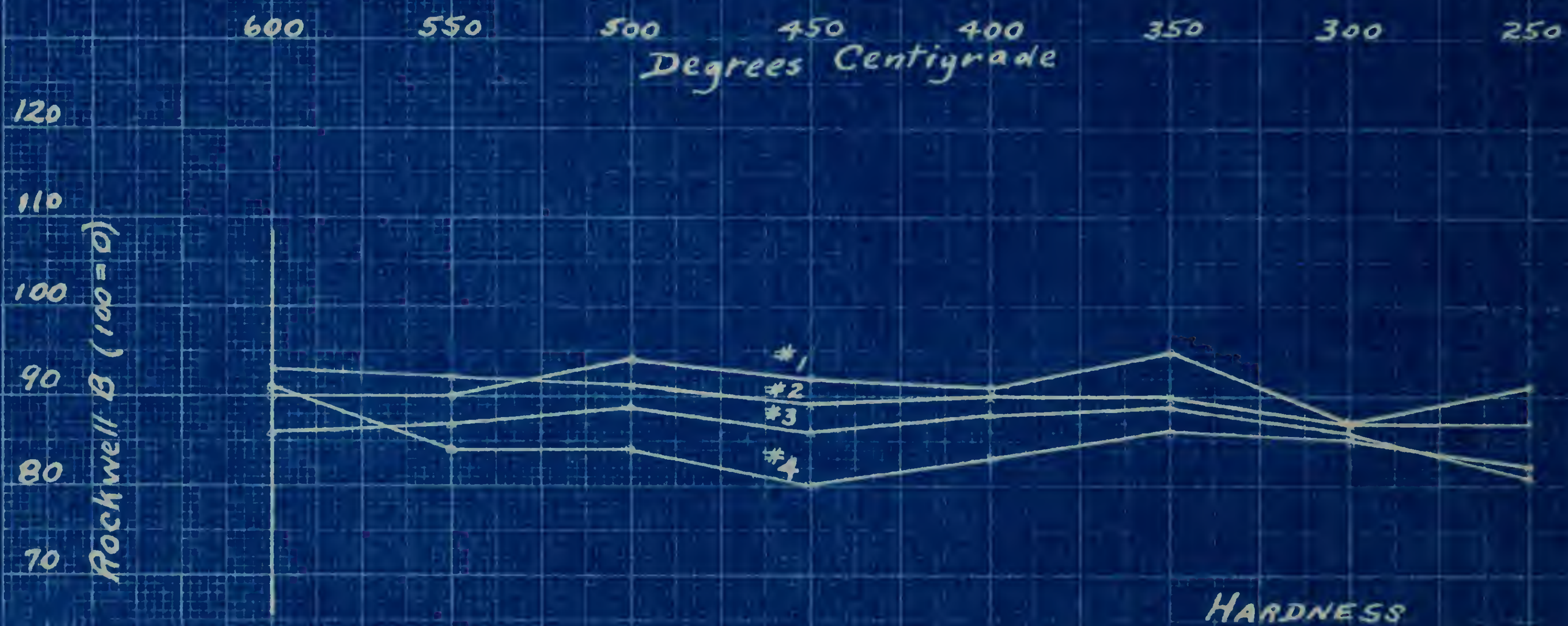
Quenched from 590°C.
Unetched X500



Alloy #2

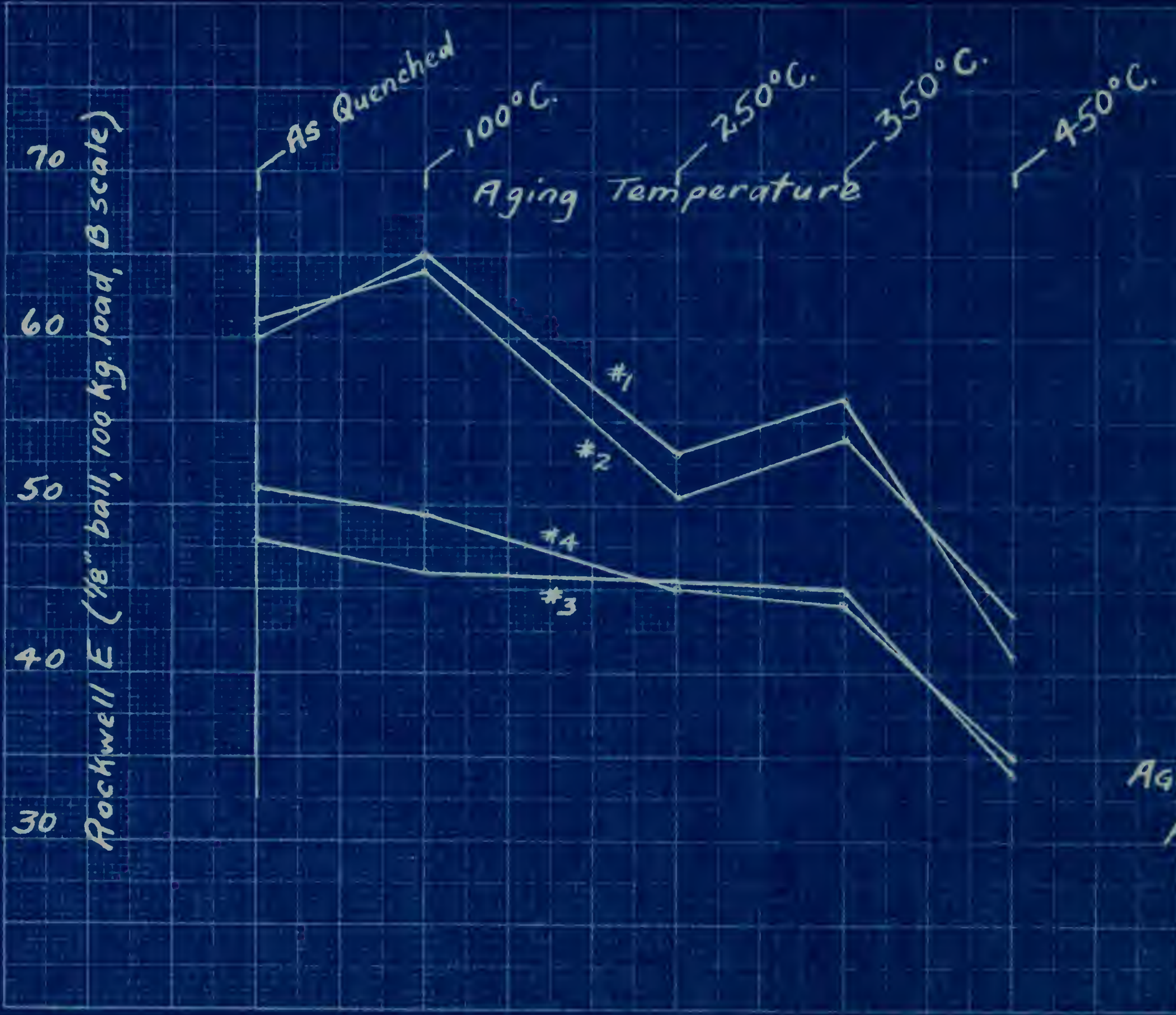
Quenched from 618°C.
1% HF etch   X500

PLATE 8



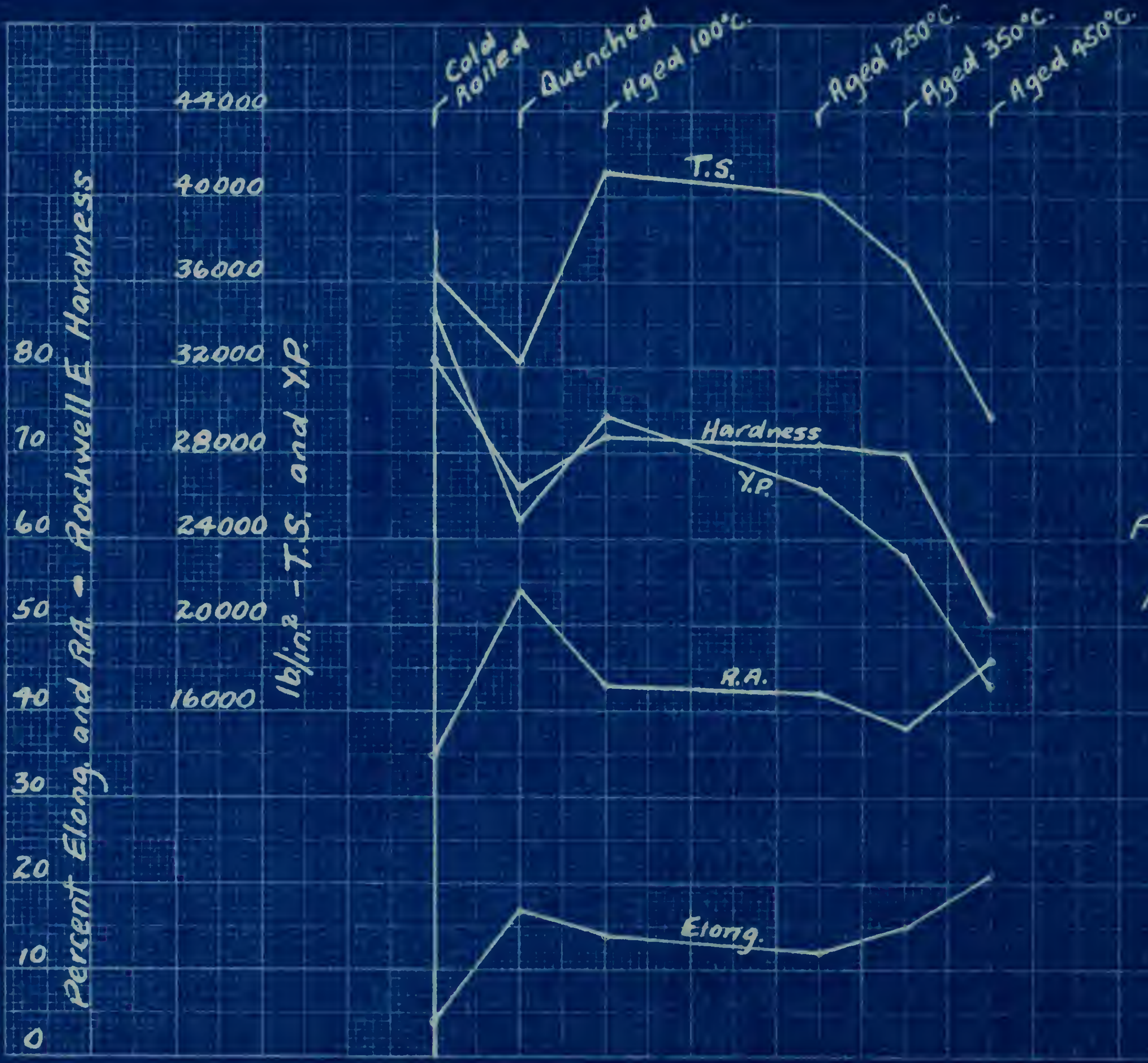
HARDNESS
VS.
QUENCHING TEMPERATURE
Alloys Hot-rolled.

PLATE 9



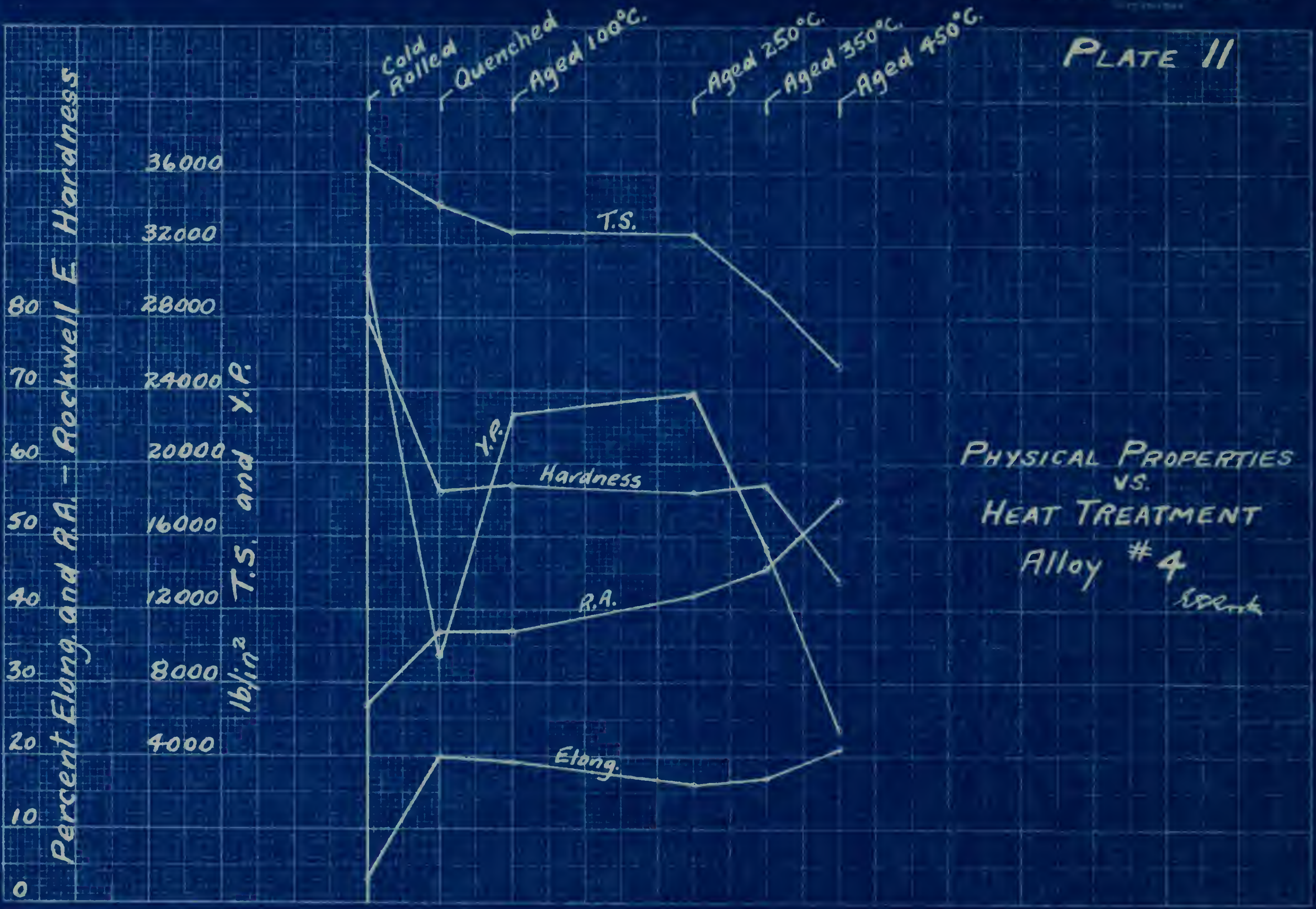
HARDNESS
VS.
AGING TEMPERATURE
Alloys Hot-rolled.

PLATE 10



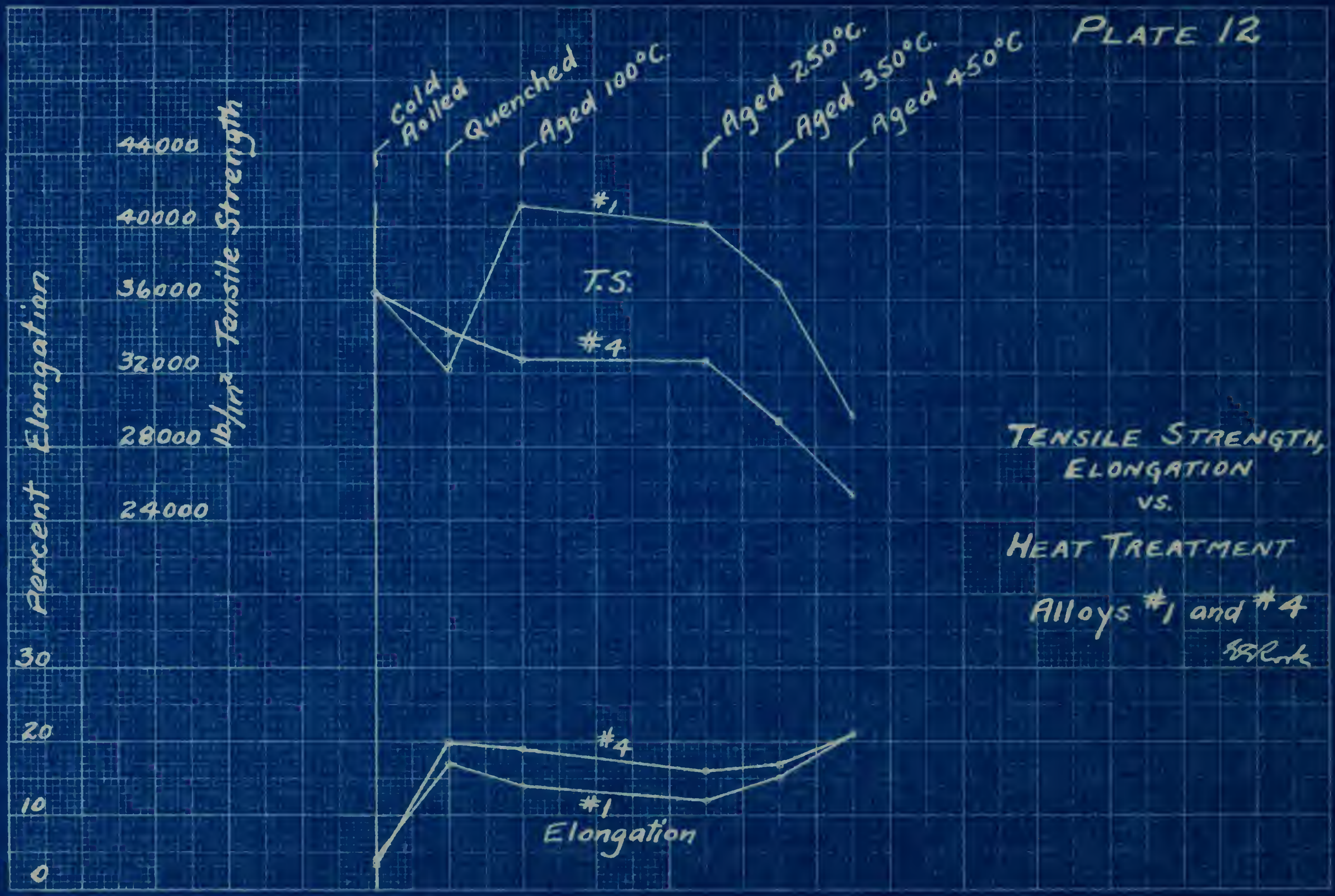
PHYSICAL PROPERTIES
VS.
HEAT TREATMENT
Alloy #1

PLATE 11



PHYSICAL PROPERTIES
VS.
HEAT TREATMENT
Alloy #4

PLATE 12

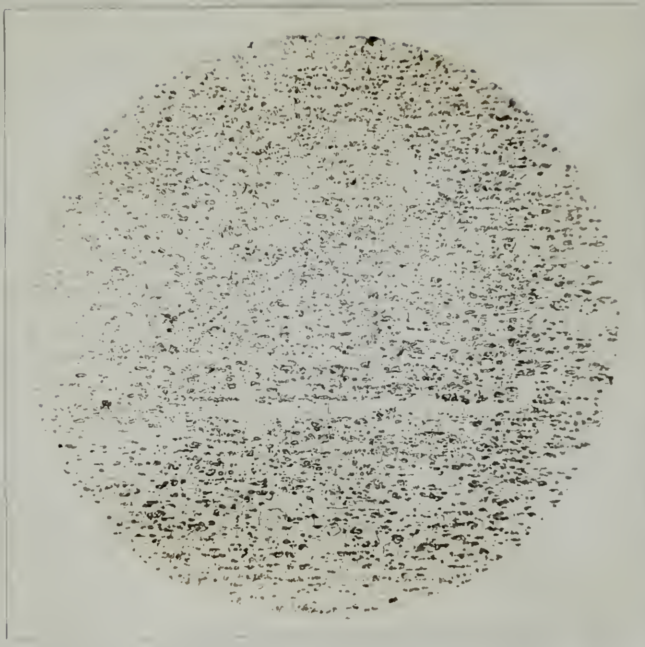


TENSILE STRENGTH,
ELONGATION
VS.
HEAT TREATMENT

Alloys #1 and #4

Alloy #1

Quenched from 590°C.
Aged at 100°C.
1% HF etch X100



Alloy #4

Quenched from 590^{o}C.
Aged at 100^{o}C.
1% HF etch X100

IV. Discussion of Results and Conclusions

11. The hardness tests of the alloys in the condition as quenched from various temperatures (see Plate 8) show nothing that can be called conclusive evidence of precipitation. It will be noted that while the hardnesses of the lower nickel alloys are consistently higher than those for the higher nickel alloys the values are practically constant over the range of quenching temperatures. The 1/16" ball (Rockwell B) is too small for this soft material but was considered satisfactory inasmuch as the results are purely relative and all hardnesses were nearly equal. The values obtained are all less than zero (Rockwell B) but assurance was obtained during the testing that the load was applied only through the ball.

In the composition range examined, the liquidus temperature decreases from 646°C. for the low-nickel alloy to 635°C. for the higher-nickel alloy (Plate 2). The solidus temperature is practically the same for the four alloys. While the rates of heating and cooling used were slightly high (4°C. per minute) the agreement between the heating and cooling temperatures indicates that any lag developed was not of serious consequence. The solidus temperature is the more important of the two because of the fact that with a rising temperature any intergranular melting will begin at that point. In the blast within the gun this would allow grains to be blown loose from the main mass of metal. If this intergranular melting is not begun it is believed that the metal, even though reduced in strength due to the elevated temperature, will have

sufficient strength to withstand the blast. Solidus temperature will also depend on amounts of impurities present. It was for this reason that the so-called high purity grade 7A was chosen as the basic metal rather than the ordinary "commercially pure aluminum." In the 51S alloy there is an excess of silicon which invites reference to the statement of Archer in Edwards, Frary, and Jeffries book[6] that the solidus in Aluminum-Magnesium-Silicon alloys having Si in excess of the Mg_2Si ratio occurs at approximately 550°C. with the freezing of the ternary eutectic. The final solidification probably takes place at a still lower temperature in 51S due to the presence of impurities. A comparison of the solidus temperatures of the subject alloys with those of the alloys 2S and 51S shows

Alloy	2S	Al-Cu-Ni	51S
Solidus temperature	658°C.	620°C.	550°C.

Thus, solidus temperature and with it resistance to intergranular melting for the Aluminum-Copper-Nickel alloys is seen to compare favorable with the 2S as against the 51S alloy.

The study of the microstructure revealed that the four alloys fall into two groups; the first group being the two low-nickel alloys and the second group being the two higher-nickel alloys. It was noted that over the whole range of temperatures from which quenched the alloys consisted of a ground mass of solid solution with scattered inclusions lo-

cated largely at the grain boundaries. These inclusions were seen to increase with added nickel but at a faster rate, i.e., there are more than eight times as many inclusions in the 4% nickel alloy as in the alloy containing ½% nickel. In the first group the inclusions were wholly the ternary compound, T^5 or Cu-Ni, as identified by the methods of Dix and Keith[8]. In the second group there appears a greatly increased amount of the ternary compound together with a large amount of $NiAl_3$. The presence of any $CuAl_2$ in any of the alloys at the as-quenched temperatures was not noted. While the short time of soaking is not sufficient to allow complete equilibrium to be reached the results obtained are believed to be qualitatively accurate. It is believed that this distribution effect is due to the normally strong attraction of nickel for copper. With small amounts of nickel present some of the copper combines with it and aluminum to form the ternary compound while the remainder goes into solution. With higher nickel content less of the copper goes to form solid solution and more forms the ternary compound until a point is reached where a large excess of nickel is needed to draw copper from solid solution in the aluminum. Nickel over and beyond this critical concentration would then unite with the aluminum and appear as $NiAl_3$. This is found to be the case for, with nickel over 1%, free $NiAl_3$ is present. Both the ternary compound and the $NiAl_3$ appear as fairly large rounded particles, mostly at grain boundaries, and would be expected to have a negative effect on physical properties. This is corroborated by the physical data for the higher-nickel alloys.

Nickel, therefore, having the power to take up and combine with all available copper to form the ternary compound as a rounded inclusion will act as a scavenger for the grain boundaries. While with proper treatment there is small likelihood of there being present any copper-aluminum eutectic, it is not an impossibility and the function of the nickel would be to draw this eutectic up into an inclusion much in the same manner that manganese is said to combine with sulphur in steel and form a rounded particle. This would remove the eutectic which might be present at grain boundaries and which, with its comparatively low melting point, 548°C., would allow early melting and disintegration.

It was originally intended to determine precisely the physical properties for the complete set of alloys with varying heat treatments. This phase of the work has had to be shortened, however, due to a lack of time. The heat-treating of the tensile specimens was done in an electric resistance furnace with the specimens buried in sand in a sheet metal container and the temperature manually controlled to offset a large temperature gradient within the furnace and a poor automatic control. It was due to lack of a close automatic control that only comparatively short time of aging was used. All tensile properties were determined across the direction of rolling. The testing machine was a Tinius Olsen 50000-pound machine using a light poise to convert it to a 5000-pound maximum load. It was run at minimum speed. Yield points were determined by the drop of the beam and noting change in rate of application of load.

To be noted on physical properties is the fact that

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To be noted in physical properties is the fact that the material hot-rolled easily and on cold-rolling showed a clean smooth finish with no tearing. The final reduction in the cold state was fifty percent.

Just as the four alloys fall into two microstructure groups so do they fall into two groups in hardness values after heat treatment (Plate 9). The two alloys of higher nickel content are slightly softer than the two low-nickel alloys and do not respond an equal amount to heat treatment. This would be expected considering the larger number of inclusions present and consequently a smaller amount of dissolved copper with the higher nickel content, just as we would not expect a one-tenth carbon steel to be as heat-treatable as one with higher carbon. It was assumed that other physical properties would likewise show a division and only the high and low nickel alloys were tested for physical properties. Plates 10 and 11 show the physical properties of the two alloys while Plate 12 shows a comparison of their tensile strength and elongations.

The solution heat treatment, i.e., quenching from near the solidus, followed by aging at 100°C., is considered to give the best combination of properties to these alloys.

Ni. content	T. S. #/in^2	Y. P. #/in^2	Elong. 2" %	R. A. %	Hardness Rockwell E
½%	41200	29700	14	43	72
4%	32700	22700	19	37	57

It will be noted that the lower-nickel alloy is the stronger and harder of the two.

12. The results comparable with those of Read and Greaves in their work on the physical properties of this system[4] show good agreement. For the 92:4:4 Al-Cu-Ni. (nominal composition) alloys:

		Present Work	Read and Greaves
Cold # Worked	Yield Point	30500	29600
	Tensile Strength	36500	36800
	Elongation	3.3	3.8
	Reduction Area	27	6.2
Annealed at 450°C.	Yield Point	5400	7200
	Tensile Strength	25400	25300
	Elongation	21	23.5
	Reduction Area	55	29.7

#Present work on sheet reduced cold about 50% in cross section to .064". Read and Greaves on 1" rod cold drawn to 7/8".

It will be noted above that the greatest disagreement is confined to those properties, Yield Point and Reduction of Area, in which positive values are difficult to determine.

The alignment of the four alloys into two groups with the division at between one and two percent. nickel which was shown by the microscope and hardness tests agrees in general with the diagram of Bingham and Haughton.[5] They place a phase boundary at between one and two percent. nickel. The liquidus temperatures also show good agreement. A marked disagreement is shown in the solidus

temperatures, however. In their determinations a great amount of difficulty was encountered in interpreting a number of minor halts in the cooling curves (inverse-rate). A close determination of solidus temperature under these circumstances is impossible but it is believed probable, as they state, that these minor halts were due to metastability in the liquid. On heating many of these retardations were not in evidence. In the present work solidus points were determined on time-temperature rather than inverse-rate curves. The inverse-rate curve, while it does gove more definite determinations, also magnifies any experimental errors to a point where they may complicate the interpretations. The uniform results obtained in the present work lend assurance to the correctness of the determinations and the later work on heat treating, i.e., the solution heat-treatment consisting of soaking at 590°C., shows positively that the solidus is above 565°C., the temperature determined by Bingham and Haughton. These variations may, of course, be due to different amounts of impurities. No explanation is attempted for the still greater disagreement in solidus temperatures for the low-nickel alloy.

13. It is reiterated here that the only test which will give positive indication of the adaptability of this group of alloys to use in cartridge cases must be actual application. We can, however, make an estimate of this adaptability by examining the above data in the light of past experiment. The alloys designedly have a low specific gravity. The only advantage an alloy of higher nickel content might have over the low nickel alloy might be the presence of $NiAl_3$.

With what may be called an excess of nickel present, it is extremely unlikely that any copper could exist outside of either the solid solution or the ternary compound. It is believed possible, however, that the smaller amount of nickel, one-half percent., is sufficient to spheroidize whatever free copper might be available as the ternary compound. Consequently, our consideration will devolve upon the low nickel alloy (95½:4:½ Al:Cu:Ni). It is composed initially to avoid the presence of any impurities which might allow earlier melting. When annealed at 450°C., its hardness, elongation, and reduction of area would indicate that it could be as easily drawn as the alloys 17S (duralumin) and 25S (silicon-manganese alloy), probably slightly more so. In the recommended heat-treated condition (quench at 590°C., aged at 100°C.) it has sufficient strength and hardness for all except rough usage. It has a solidus temperature comparable with that of the commercially pure aluminum, which, while not high, might be sufficiently elevated to prevent disintegration. At elevated temperature however, it is extremely soft and care must be taken when heat-treating not to strain it in any manner. Evidence of this softness occurred in attempting to heat-treat a specimen made up of laminations screwed together. The strain on the screw-head caused it to sink deeply into the outer metal when the metal was heated prior to quenching. Whether or not this softness will cause failure in the cartridge case during the firing is a subject for conjecture. Alloy 51S was not extruded into the extractor recess as much as alloy 2S and at the same time alloy 2S did not suffer from disintegration to

to the same extent that the 51S did.[2] It might be expected that the Al-Cu-Ni alloy would resist disintegration equally as well as the 2S and that it would resist extrusion as well as the 51S.

The general conclusion is that a trial of this alloy in actual use would be worthwhile. It is not a conviction that it will be more adaptable than the standard commercial alloys but there is in its favon as against them, the difference in impurities and absence of alloying additions which might allow earlier melting.

14. A continuation of this work along the following lines would be advisable: (1) Testing of the chosen alloy by actual application (Commercial application of an alloy based on grade 7A aluminum would not be practical. But while it is desirable to have impurities a minimum, it is believed possible that use of a commercially practical high-purity grade of aluminum would give satisfactory results); (2) Determination of the physical properties of the two intermediate alloys of this group, noting any critical nickel content which would be expected at between one and two percent.; (3) Further determination of solidus temperatures working with alloys having varying amounts of impurities purposely added; (4) Further determinations of effects of heat-treatment involving a variation in time of aging, and quenching from temperatures below that used in the present work.

V Appendix.

15. Relative References and Notes.

1 Note: Fixed ammunition is the term applied to the charge for a gun where the propellant is contained in a cartridge case which is fixed to the projectile, the two constituting a unit mass; e.g., all pistol ammunition is fixed ammunition.

2 "Report on Conditions Developed in the Firing of Aluminum Cartridge Cases", Naval Gun Factory Report, 18 April, 1929, C.E.Margerum.

3 "Light Metals and Alloys, Aluminum, Magnesium", Circular of the Bureau of Standards, No. 346.

4 "The Properties of Some Aluminum-Nickel and Copper-Nickel-Aluminum Alloys", Read and Greaves, J.Inst.Met.,13,100-159

5 "The Constitution of Some Alloys of Aluminum with Copper and Nickel", Bingham and Haughton, J.Inst.Met.,29,71

6 "The Aluminum Industry", Edwards, Frary, and Jeffries, Vol.2, Aluminum Products and Their Fabrication.

7 "Metallurgy of Aluminum and Aluminum Alloys", R.J.Anderson.

8 "The Etching Characteristics of Constituents in Commercial Aluminum Alloys", Dix and Keith, Proc.A.S.T.M.26

9 2S Aluminum Co. of America commercially pure (99% +) aluminum, principal impurities iron, silicon, and copper.

10 51S Aluminum Co. of America alloy. Nominal composition: 1% silicon,0.6% magnesium, remainder aluminum plus impurities.

11 7A Aluminum Co. of America highest purity (99.95%) aluminum.