T H E S I S

INVESTIGATION OF METHODS IN CASE CARBURIZATION OF STEEL.

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INVESTIGATION OF METHODS IN CASE CARBURIZATION OF STEEL.

In general the subject of Heat Treatment covers too wide a territory to be discussed in this limited study.

But, the common chemical and mechanical forms of iron and steel have a direct bearing on all heat treatments in so far as their characteristics influence the consumption of carbon.

Referring to equilibrium diagram (Roberts-Austen) the action of iron of different carbon content, when heated, can be readily discussed and understood.

First considering the hypo-eutectoid, iron carbon alloys, which contain very little carbon -0% to 0.9% carbon- we have a ferrite known as an "alpha-iron". Upon heating the alpha ferrite to a little over 1400° F. the "Beta-iron" begins to form, the temperature varying inversely as the carbon content. Beta Iron is a non magnetic substance. Heating the beta form to the upper critical point or the point of solidification we have what is known as "Gamma-iron". Gamma Iron is of a soft nature and has the property to take up carbon very readily in chemical combination. This property is not possessed by the alpha iron. The gamma iron critical point

is governed by the carbon content and goes into the eutectoid and hyper-eutectoid alloys.

Steel is an alloy chemically composed essentially of iron and carbon. Of course, certain impurities are present in all steels, such as silicon, phosphorus, sulphur and manganese. The carbon content will vary within certain limitations. It cannot exceed 6.67% because; three (3) parts iron and one (1) part carbon produces a satisfied condition; Fe_3C. The atomic weight of iron = 55.85, of carbon = 12, Fe_3C = 179.55. Therefore the percent carbon is (12 x 100) ÷ 179.55 = 6.67%. This proves our limiting condition, chemically; and any excess of carbon must be in a free state known as graphite.

If a bar of steel be heated above the critical temperature (about 1280° F. as shown on the diagram) and allowed to cool slowly we have; first Cementite + Austenite, then Cementite + Austenite + Graphite, then Cementite + Ferrite + Graphite. This shows that on cooling slowly the steel has a tendency to revert to its natural elements. But if we "quench" the specimen above the critical point the temperature change is so quick that chemical restoration cannot be accomplished and we have a product of heat treated steel.

It has been determined by experiment that the temperature change in a piece of steel is proportional to the heat added up to a certain point and at that point

no rise in temperature can be detected for a short time, although we still add heat. This point is known as the critical point and occurs at or about a cherry red. At the critical point the steel loses its magnetic properties. When cooling starts the temperature will fall, since heat is given off, until a point is reached where the temperature does not change for a short time, this point is slightly lower than the critical point in heating. This point is known as recalesence point. The critical point on heating is commonly known as the decalesence point. Theory teaches us that the heat consumed in passing the critical temperature is used in producing the chemical transformation and a like amount of heat is given off by chemical reaction on the decline.

Experience shows that before we reach the decalesence point we cannot force the steel to assume different properties. But after we pass this point it is very easy to cause a chemical, as well as mechanical change, in the steel to become permanent. For example; take a piece of carburized steel and heat it to 1800° F. and "quench" it. We have changed the specimen from a ferrite + graphite to a cementite + ferrite or a pearlite. This is commonly called hardening without reference to refinement.

To refine a chemically uniform steel, we must determine its critical point and heat to a point just above it and "quench" at this temperature. Microscopic

3000°F

LIQUID SOLUTION OF IRON & CEMENTITE

MOLTEN METAL

F=3-1=2

Solid solution forms Austenite

F=3-2=1

Fe₃C + gamma iron Saturated Austenite

Cementite begins to solidify

Fe₃C continues to solidify

2000°F

1 SOLID SOLUTION OF AUSTENITE + CEMENTITE (Fe₃C

F=3-2=1

SOLID SOLUTION OF Austenite

F=3-1=2

2 AUSTENITE + Fe₃C + GRAPHITE

F=3-2=0

Fe₃C begins to be liberated from Austenite

B iron forms

α iron forms

B IRON CONTINUES TO FORM.

α IRON CONTINUES TO FORM

TEMP. F.

1000°F

1. FERRITE + CEMENTITE

F=3-2=1

2. FERRITE + GRAPHITE

F=3-2=1

3. FERRITE + CEMENTITE + GRAPHITE

F=3-3=0

← STEELS → ← UNDEVELOPED → CAST IRON → ← UNDEVELOPED →

← HYPO-EUTECTOID STEEL → ← HYPER-EUTECTOID STEEL → ← HYPO-EUTECTOID CAST IRON → ← HYPER EUTECTOID CAST IRON →

.5% 1% 1.5% 2% 2.5% 3% 3.5% 4% 4.5% 5% 5.5% 6% 6.67%

% C.

■ - IRON CARBON STRUCTURAL AND EQUILIBRIUM DIAGRAM - ■

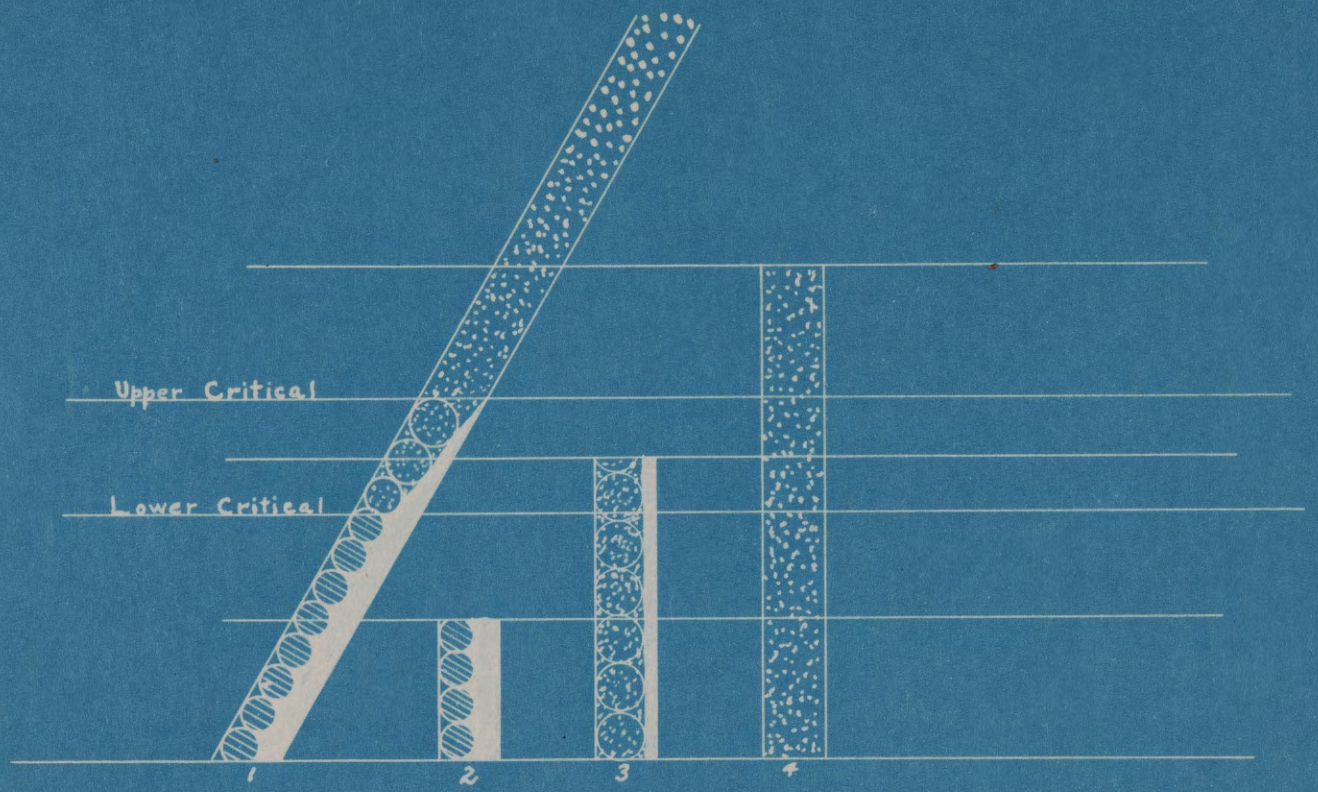
examination will show that this temperature will give us a steel of fine grain and sclerescopic examination will show extreme hardness, if the steel is of high carbon content. If this temperature is exceeded a coarse grained brittle product will be formed. Often this mistake, alone, defeats the object of heat treating. Another common error is to allow the temperature to go above the specifications and hardening at the proper point on temperature decline. This does not refine. In order to correct the mistake the temperature must fall below the critical point and be heated to the proper point and "quenched".

The critical point of steel falls as the carbon content increases, due to the low burning point of carbon.

Too much stress cannot be placed upon the study of each variety of carbon steel and its critical point, if good results are to be expected.

If the steel is of varying compound, initial heating is mandatory if a good result is required; for strains will be caused by the varying carbon content. The specimen will be interspersed with hard brittle spots, thus weakening the product. In a careful preheating, the pieces should not be placed in a hot furnace, but heated slowly to allow a chemical readjustment to take place before the hardening process begins.

Referring to a diagram, Figure 138, from Bullens, "Steel and Its Heat Treatment", slanting specimen shows very clearly the internal action of heating and "quenching" a piece of carbon steel. The small circles of cross hatched area show a pearlitic composition and the blackened area shows free ferrite. Number two shows that "quenching" at a temperature below the critical point will produce no change in structure, therefore no change in hardness. The area between lower and upper critical points shows the pearlitic structure changing into a solid solution, absorbing some of the ferrite, up to the upper critical point where it is all absorbed. Number three is a specimen "quenched" while passing through the decalesence point and it has a slight change in structure with an increase in hardness. Number four shows a "quenching" after it has passed the critical point with a fine grained structure and a complete absorption of the free ferrite. This gives a refined, hard product. If the temperature is allowed to rise the crystals grow larger and "quenching" at a high temperature will give a brittle product. This clearly illustrates that the most effective point exists just after the upper critical point is passed.



Changes in Carbon Steel on Heating and Quenching. (Bullens)

Geo. H. Irish.

To confine our treatise of carburization to case hardening we must abandon the assumption that our steel has its carbon content and enter into a comparison of the methods used in the carburization processes. All the methods are not described herein for we will confine our efforts to actual experimental data produced for this subject.

The object of case hardening is to produce a hard wearing surface and still retain the toughness of the metal as in the "core". We know as the hardness increases, so does brittleness and tensile strength decrease. We defeat this physical fault by just hardening the surface and retaining the "core" toughness.

The heating of the specimens was conducted in a No. 16, American Gas Furnace with producer gas. The air supply was generated by a small pump driven by a motor. Throughout the tests, as near as possible, a neutral flame was maintained in order to prevent any oxidizing or reducing effect on the steel. This was also done to prevent the burning of the reducing agent. If the flame has any excess of gas there will be a limited amount of carbon that is not burned by the air supply and this will be absorbed by the iron, because at temperatures above the critical point iron has an affinity for carbon. If there is any excess of air the hot air will burn or

oxidize the red hot steel and the carbon cannot enter the pieces through a crust of oxides.

The different methods of carburization are nothing more than a variety of ways to introduce the carbon into the steel. Heating the specimen in an air tight container with carbon will produce very little effect in carburization, but allow a small amount of air to be present; the oxygen will unite with the carbon forming a monoxide gas CO and this coming in contact with the pieces will give up some of its carbon as : $2CO = CO_2 + C$. Then the carbon in turn regenerates the gas into the monoxide. This can go on indefinitely with a small amount of air. An excess of air will produce oxidation, showing that a neutral flame - in the case of a gas furnace- is imperative.

All of the specimens used in these tests were taken from the same piece of cold rolled steel of 1/2" diameter. The carbon containers were pieces of 1-1/2" pipe 6" long with caps for end covers. A small hole was bored in one end of each cap, just large enough to admit the end of the pyrometer coupling. The furnace used was of the Oven Type of the American Gas Furnace Co. and was heated with producer gas.

The first test run was with wood charcoal to determine the penetration properties. The pieces were placed in the pipes and covered with charcoal. These

were placed in the furnace and allowed to remain at 1700° F. for a definite period; specifically one (1) to eight (8) hours inclusive. One specimen was run at each hour intercal, keeping the temperature constant. The pieces were allowed to cool in the containers, thus annealing them to facilitate cutting and polishing for microscopic examination and measuring the penetration.

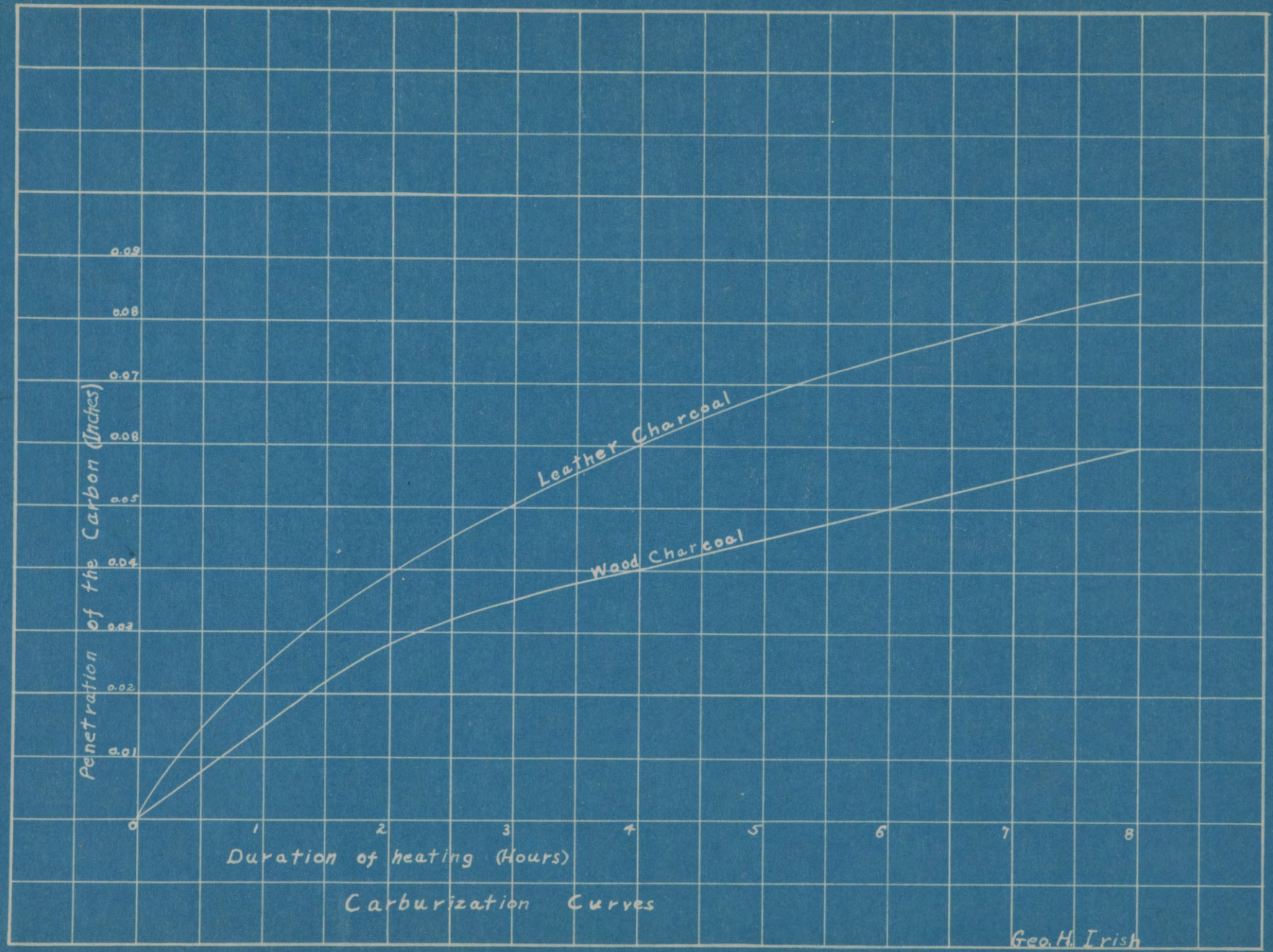
The leather charcoal tests were handled in the same manner.

To measure the penetration it was necessary to polish one end and etch the polished surface. The carburized portion of the surface, after etching, is a different color from the unaffected portion or the "core" of the specimen. The color variation is governed by the method of etching. First, the end was cut off to eliminate the end longitudinal carburization, an even surface ground on the emory wheel, then on a coarse emory disc, on a fine emory disc and finished on a buffing wheel, with a valve compound. In each operation cutting marks were made at right angles to the process preceeding making sure, each time, that all the marks were taken out. This produced a surface smooth enough for all practical measuring purposes.

For etching, the following concentrated nitric acid method, recommended by Sauveur was adopted. His instructions as published in, "The Metallography and Heat Treatment of Steel", are as follows: "The polished

specimen conveniently held with a pair of pinchers (preferably with platinum tips) should be dipped in a beaker or other vessel containing concentrated nitric acid (1.42 specific gravity) and immediately afterwards held under an abundant stream of running water. When iron is immersed in concentrated nitric acid it assumes a passive state, that is it is not affected by it. As soon, however, as the layer of concentrated acid which covers the polished surface is diluted with running water, the steel is vigorously attacked but for so short a time (since the water removes all traces of acid) that there is little danger of etching too deeply. One such treatment is generally sufficient to bring out the structure sharply and clearly but if the specimen is found insufficiently etched, the etching should be repeated in the same manner. The author believes that the simplicity of this etching treatment and the excellent results generally obtained have been overlooked by Metallographists".

The measurements were made with a scale graduated to one one-hundredth of an inch, making use of the reading glass. It is easy to read to 0.005 of an inch by using the glass and the penetration is taken as the mean of several measurements taken at intervals around the specimen. The results are compiled as follows and graphically illustrated on page #12.



Carburization Curves

Geo. H. Irish

WOOD CHARCOAL		LEATHER CHARCOAL	
Time of Heating (Hours)	Penetration (Inches)	Time of Heating (Hours)	Penetration (Inches)
1	0.015	1	0.025
2	0.028	2	0.040
3	0.035	3	0.050
4	0.040	4	0.060
5	0.045	5	0.070
6	0.050	6	0.075
7	0.055	7	0.080
8	0.060	8	0.085

The results as obtained show leather charcoal more efficient than wood charcoal, giving us a quicker and deeper penetration for same time interval.

Our next attempt at case carburization was entering a more or less theoretical field, making use of and Oxygen-Acetylene torch.

At first thought, after recognizing the fuel qualities of acetylene C_2H_2 we can readily assume if we can devise some means of producing a reducing flame in the presence of the heated specimen, case carburization may be accomplished.

An ordinary No. 8 Oxweld head was used for this work. With a neutral flame the possible temperature is 6300° F. at the tip. The pieces were heated by use of the torch and after a good temperature (approaching white heat) was obtained an excess of C_2H_2 was turned on. The oxygen and air supply not being sufficient to burn all of the acetylene, there remained an excess of carbon

to be dissipated. Naturally some of it was absorbed by the steel.

Each piece was first heated and then held in the reducing flame for 2, 5, and 10 minutes, respectively. No effort was made to relieve the strains in the specimen but each was "quenched" with casing heat. Each piece was tested under the sclerescope with the following results:

Sclerescopic readings from specimen subjected to carbon flame for 2 minutes.

40, 25, 35, 20, 35, 10, 10, 15, 15, 15, 15, 15, 20, 20, 25, 35, 20, 25, 35, 30

Sclerescopic readings from specimen subjected to carbon flame for 5 minutes.

25, 20, 20, 30, 30, 50, 45, 35, 35, 30, 25, 25, 40, 25, 50, 30, 30, 35, 25, 20

Sclerescopic readings from specimen subjected to carbon flame for 10 minutes.

30, 25, 20, 30, 35, 20, 30, 25, 25, 40, 25, 30, 40, 45, 50, 50, 35, 35, 35, 15

This clearly illustrates the fact that the tests were far from a success. Due to the variation in hardness strains were set up in each piece causing a warping. An effort was made to eliminate this fault by subjecting the reverse side of the specimen to the same carbon treatment as before. This effort was a partial success but the warping could not be eliminated. The untreated specimens gave a sclerescopic test of 10. This shows that

some points were highly carburized while others were scarcely affected. This may be due to the fact that an oxide scale was formed in preheating, stopping the absorption of carbon in spots.

With the present knowledge of acetylene carburizing, the method is not a success and is of no commercial value.

Our next tests were conducted with cyanides to produce intense superficial hardening. Giolitti disapproves of the use of cyanide, because the cyanogens do not exist already in natural forms and the pure formation with some other element must be fused with the hot metal to produce a very superficial case. He further states that the carbon monoxide gas is so far surperior to the cyanogens that the qualities of the volatile cyanides is almost negligible for commercial use.

In Cyanide Hardening the methods may be classified in two ways, sprinkling and immersion. In sprikling, the heated specimen was placed in and covered up with the cyanide used, and allowed to cool there in the pulverized cyanogen salt. In immersion, the specimen was subjected to a liquid bath of the fused cyanogen salt.

The cyanides were heated to 1500° F. - 1600° F. and the red hot specimen dropped into the crucible and allowed to remain there for a definite period and "quenched" from that temperature. Cyanides are very dangerous

and care must be taken in their use for if it gets into a frest cut it will prove deadly. There is also great danger from the gases, and a face mask should be provided if work is carried on in an open furnace.

In the experiments sodium cyanide and cyanide chloride were used. In sprinkling, two tests were made with one and two sprinklings, respectively. The specimens were heated in the gas furnace and covered with the salts, and allowed to cool in the open. The pieces were then heated and hardened at 1500° F.

In the immersion tests the cyanogen salts were fused in small crucibles and the heated specimens were dropped into the liquid and allowed to remain there for 5, 10, and 15 minutes, respectively. They were then taken out and "quenched" at the casing temperature.

Sclerescopic tests were made on all the pieces with the following results.

Method	Sclerescopic Reading.	No. of Times.	Cyanide Used
Sprinkling	24	1	Sodium Cyanide
"	30	2	" "
"	27	1	Cyanide Chloride
"	28	2	" "

Method	Sclerescopic Reading	No. of Minutes	Cyanide Used
Immersion	35	5	Sodium Cyanide
"	38	10	" "
"	40	15	" "
"	30	5	Cyanide Chloride
"	35	10	" "
"	40	15	" "

An examination of results will show very little difference in the use of the two cyanides excepting that the sodium cyanide was a little more efficient due to the fact that it contained 52% of cyanogen while the cyanide chloride contained 40%.

By observation during experiment; the cyanide chloride was proven to be more volatile and passed away as a gas much faster than the sodium cyanide. These facts alone recommend the use of sodium cyanide in preference to cyanide chloride.

It will be well to devote a small study to the refinement of case hardened steel. As has been proven the higher carbon steels have a lower decalesence point. Therefore, if we attempt to refine a piece of steel with a surface of higher carbon content than the center, when the "core" is ready for refining the surface will have passed the critical point and have the large crystal formation, when "quenched" to refine the "core". It will be necessary to heat again through the surface critical point and "quench" to get a refined surface. This second heating will produce no material change in the center, due to the fact that the decalesence point has not been reached.

From the results obtained in the foregoing tests we will recommend the following measures for practice. (1) The use of leather charcoal in pre-

ference to wood charcoal is recommended because the monoxide gas from leather charcoal has more penetrating properties. (2) The use of acetylene in case carburization is not reliable since the results obtained are far from satisfactory. (3) There is no great distinction in the two cyanide methods used. The results obtained were, with each, very nearly the same, but the sodium cyanide is preferable because it contained more cyanogen. (4) The use of the carbons with the monoxide gas is far superior to the other methods and should always be used, except where a quick superficial case is desired. (5) When superficial cases are satisfactory or a variegated color is desired we can use the cyanides to an advantage.