THESIS.

THE CAUSE OF FAULTS IN ELECTROPLATED SPRINGS.

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Submitted by

Course XIV.

INDEX.

THE CAUSE OF FAULTS IN ELECTROPLATED SPRINGS.

The electroplating of steel springs, in certain baths, has been known for a considerable length of time to be impossible in commercial practice. This is because the springs are rendered so brittle as to be useless. They sometimes break in the bath under the slight tension necessary to keep them stretched so that the plate will not bridge across from turn to turn. In any case , they are easily broken by pulling apart after the immersion in the bath. The cause of the phenomenon is un known, and apparently no investigator has attacked the problem, since no mention of it has been made in any of the electrochemical or physical literature.

In order to proceed systematically, it was first necessary to find out the conditions under which the springs broke. These conditions were found by varying the bath, the temperature, and the current-density. Since cleaning and pickling are necessary in any commercial plating operation, it was thought desirable to see if these operations had any effect on the elasticity of the springs.

The first thing found was that the breaking effect is not so universal as had been supposed. This conclusion was arrived at by considering the following series of experiments with various baths. The first bath which was used was the ordinary nickel-plating bath. This was made up as follows:

$NiSO_4 . (NH_4)_2SO_4 . 8H_2O$ - - -	70 grams
$(NH_4)_2SO_4$ - - - - - -	10 "
Water - - - - - -	1 Liter

The solution for removing grease was made by dissolving 120 grams of sodium hydroxide in one liter of water. The pickling solution was 150 cc. concentrated sulphuric acid in 750 cc. water.

Several sizes of steel wire, made especially for springs and listed in Edgar T. Ward & Sons'price-list as " Black Tempered Spring Wire ", were procured and coiled into springs. These were placed in the bath and plated as follows:

Diam.	Time plated	Current
1.05 mm.	1 h. 25 m.	0.20 amp.
1.33 "	1 h. 37 m.	0.25 "
1.65 "	2.h. 7 m.	0.35 ".

Samples of piano-wire, which is very similar to spring-wire, were plated as follows:

Diam.	D. after plating	Time plated	Current
0.28 mm.	0.45 mm.	1 h. 10 m.	0.12 a.
0.33 "	0.50 "	1 h. 28 m.	0.15 a.

All these runs were carried on at room temperature.The springs were absolutely unaffected in any way. The nickel plate was firmly adhering and could even be burnished. When the springs were stretched beyond the elastic limit, the nickel plate cracked and peeled.

The regulation copper-plating bath was next made up. This had the following composition:

$Cu_2(CN)_2$ - - -	35 grams
NaCN - - -	140 "
Water - - -	750 cc.

Sodium cyanide instead of potassium cyanide was used in all these experiments on account of the present scarcity of potassium salts. A sample of piano-wire, 0.46 mm. in diameter, was plated with 0.45 amperes. It was held in the bath under tension and broke at the end of twenty-two minutes. No copper was deposited, owing to too low a voltage. This would indicate that the hydrogen instead of the copper caused the trouble. A sample of the spring-wire 1.05 mm. diameter was plated with 6.15 amperesand a good deposit of copper obtained. At the end of twenty minutes it was removed from the bath and easily broken by stretching. Larger sizes, and springs of different metals were unaffected. These data are as follows:

Diam.	Material	Time plated	Current
1.57 mm.	Steel	25 m.	10.00 amps.
2.02 "	"	"	" "
2.54 "	"	"	15.00 "
0.53 "	Brass	21 "	10.00 "
1.03 "	"	30 "	" "
0.64 "	Phosphor-bronze	27 "	" "

What length of wire

In order to test the effect of the hydrogen deposition, springs were electrolyzed in a solution of sodium hydroxide (80 gms. NaOH, 430 cc. H_2O)

Diam.	Time plated	Current
0.33 mm.	35 m.	1.50 amps.
0.46 mm.	49 m.	5.00 amps.

All springs were unaffected, showing that the hydrogen has no effect under these conditions.

The pure sodium cyanide bath was next tried. In order to prevent the escape of the poisonous cyanogen gas, copper anodes were used at first, with no attempt to keep the anode and cathode compartments separate. Inconsistent results were obtained, as follows:

Diam.	Time plated	Current
0.29 mm.	38 m.	1.50 amps.
*0.46 mm.	9 m.	7.00 amps.
1.01 mm.	1 h.	14.00 amps.

The asterisk marks the one that broke. The inconsistency can probably be explained from the fact that the solution was used over and over again. Copper was deposited onthe springs. To prevent this, the copper anode was placed in a porous cup, such as is used in a Daniell cell. This was tried alone, and in series with a regulation cuprocyanide bath, but the results did not agree with previous runs in that no springs broke whatever.

Diaphragm cell alone

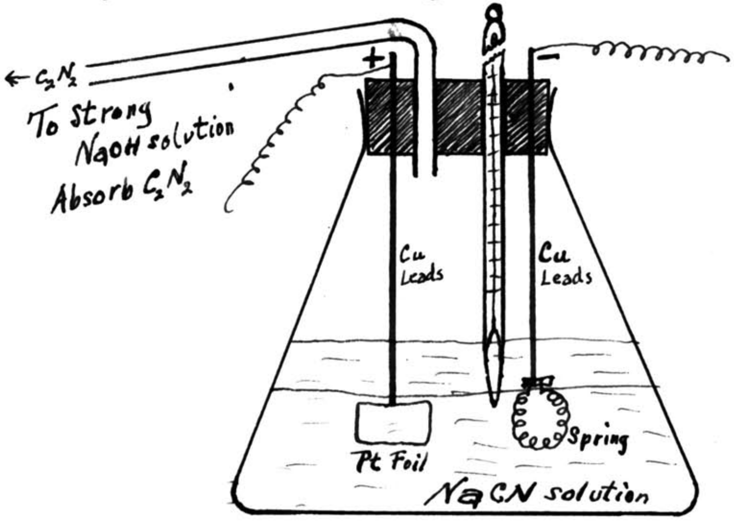
Diam.	Time	Temp.	Current
0.33 mm.	1 h. 15 m.	110-120° C.	2.5 amps.

Diaphragm cell in series with cuprocyanide cell

Diam.	Time	Temp.	Current
0.33 mm.	20 m.	40° C.	3.5 amps.
" "	35 m.	95° C.	7.0 amps.

The copper deposited even with the diaphragm cell, so that a platinum anode was decided upon, and the cyanogen was to be lead out of the vessel into an absorbing medium.

The cell used in all following electrolyses embodied these ideas. It consisted of a large, wide-mouthed Erlenmeyer flask, provided with a two-holed rubber stopper. Two copper leads pierced the stopper. To one was attached the platinum anode, to the other was attached the spring to be electrolyzed. One of the holes in the stopper accommodated a thermometer, the other held the delivery-tube which removed the cyanogen. The cell is shown diagrammatically in the following sketch.

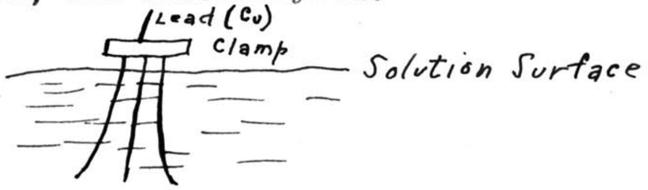


With this cell in series with a cuprocyanide cell, electrolysis of the spring, in both pure cyanide and in cuprocyanide, could be carried out under exactly identical conditions. The 0.46 mm. piano-wire was electrolyzed for ten minutes at 7.0 amperes. The sample which was in the pure cyanide could be easily broken, while the sample in the cuprocyanide was much more difficultly broken. This shows that the pure cyanide has the greater effect, and it was decided to carry out all further electrolyses in the above cell, using pure sodium cyanide solution.
made slightly alkaline with NaOH

Omitted data.

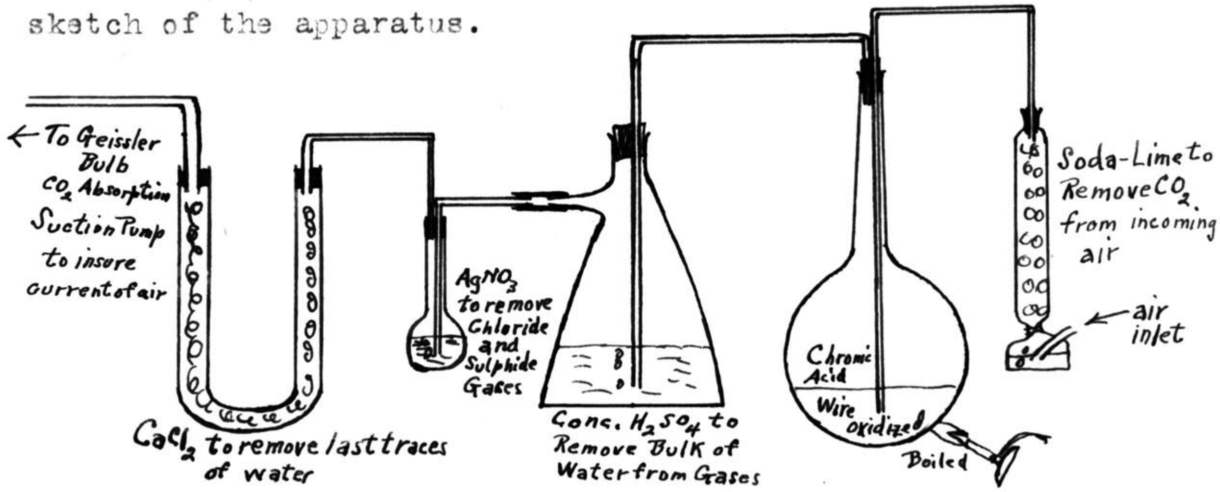
In regard to the data on page 4, a sample of the 0.46 mm. spring was hung up, under tension, in the cyanide bath and left for two hours, with no current passing. Its properties were not affected in any way, showing that the electric current is a necessary factor in the effect.

Also three pieces of the wire were held as in the following sketch, and electrolysed.



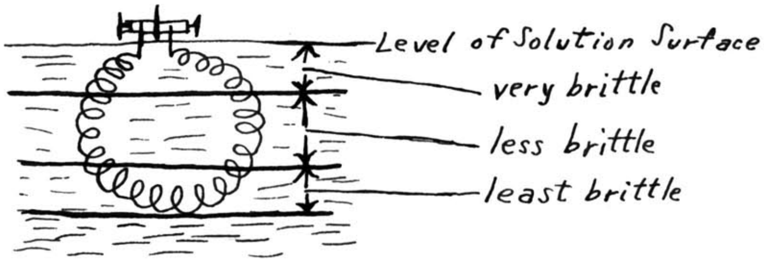
The current was 3.00 amperes, which is one ampere for each wire, and the time of immersion was twenty-three minutes. The wire was just as brittle after this treatment as it was if it had ~~been~~ first been coiled and then plated. This shows that coiling is not necessary in order to have the effect take place, but all following experiments were performed on coiled springs since more wire could be put in a given space with that arrangement.

The above experiments show conclusively that the cyanide radical is necessary to produce the breaking effect. This suggests a sort of case-hardening effect, but as all of the electrolyses are carried out at temperatures less than the boiling-point of water, such an effect seems highly improbable. Nevertheless, it was thought desirable to get some information regarding the carbon-content of the wire. The carbon was determined before and after electrolysis by means of the chromic acid method. (Treadwell-Hall, 1914 ed., p. 399) The wire is boiled with chromic acid to oxidize the carbon to carbon dioxide, which is absorbed in a weighed Geissler bulb. The following is a sketch of the apparatus.



The first analyses showed an average of 0.35% carbon for the untreated wire, and values of 0.70%, and 1.22% for the wire that had been electrolysed. These values are very unreliable, however, because the analytical apparatus was not working well. The wash bottles shown above were too small, at first, for the volume of gases and vapors which had to pass through them, and caused trouble by filling up and overflowing.

But when the small wash-flasks were replaced by ones of suitable size, the analytical apparatus gave no further trouble, and good checks were obtained. The brittleness seems to be a function of the depth of immersion, for the parts of the spring nearer to the top of the solution seem to be more brittle than those parts more deeply immersed.



It was also noticed in these runs that a very strong odor of ammonia was present at the end of every run. The colorless solution also grew dark-brown around the anode, and this coloration soon diffused through the entire solution. The following are the analytical data.

Before Electrolysis.

	I	II
Weight sample	2.1945 grams	2.6765 grams
Wt. Geisslers	57.7215 grams 57.6650	57.7962 grams 57.7195
Wt. CO_2	0.0565 grams	0.0767 grams
% C=	$\frac{0.273\times5.65}{2.19}$ = 0.70	$\frac{0.273\times7.67}{2.68}$ = 0.78

Average = 0.74% C

After Electrolysis.

See next page.

After electrolysis.

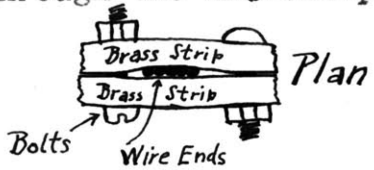
	I	II
Weight sample	1.1719 grams	1.3274 grams
Wt. Geisslers	57.8295 grams 57.7983	57.8628 grams 57.8310
Weight CO_2	0.0312 grams	0.0318 grams
% C	$= \frac{0.273 \times 3.12}{1.17} = 0.73$ %	$\frac{0.273 \times 3.18}{1.33} = 0.65$ %

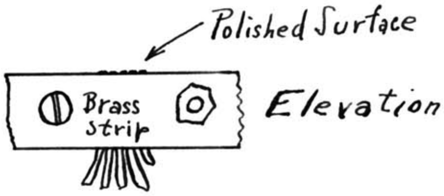
Average = 0.69 %

These results(0.74 and 0.69) check within the limits of analytical error, so that we may say that the carbon-content does not change. This particular sample was 0.46 mm. in diameter, and was electrolysed at 80-85° C. with 3.5 amperes for one hour and fifteen minutes. The dark-brown coloration and the strong odor of ammonia were in evidence as usual.

Since the carbon-content did not change, it was thought that there might be a chance of the structure of the steel changing. In order to investigate this, specimens were prepared for microscopic examination. On account of the small size of the wire, special methods of preparation had to be used. Several lengths of the wire were clamped between two strips of brass in such a manner that the ends projected beyond the surface of the brass. These ends were then ground down flush with the brass surface and the whole surface, brass and steel, was ground and then polished with rouge. In this manner several ends of the wire were exposed for the microscope. The arrangement is shown in the following sketches. (See next page)

The plan view of these sketches is the one seen through the microscope.





The springs were etched with a four percent solution of nitric acid in alcohol. The examination showed no noticeable difference between the structure of wire which had been electrolysed and that which had not been. The microscope was fitted with a camera attachment, so that photomicrographs could be taken. This was done, and the pictures are shown on the next page. The picture of the electrolysed spring appears slightly different from that of the other, but the difference is not in the structure. It is probably caused by improper developing or fixing, or the plate may have been slightly jarred during exposure.

The effect of annealing the wire was next studied. This operation was carried out in an electric furnace of the resistance type. A can was filled with some heat-insulating material, and a helix of nichrome wire was inserted in the center. The furnace was designed to study the metal-fog in fused electrolytes, and had a sight-tube which was in the right position for the insertion of a pyrometer. The general arrangement is shown in the sketch. For sketch and annealing data see page 12.

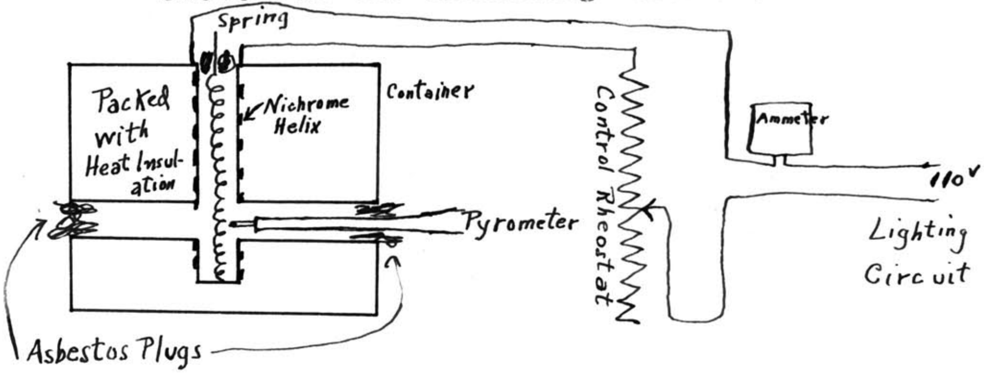
Magnification 175 Diam.

Photomicrograph of wire
which has not been electrolysed.
0.7 % Carbon

Magnification 175 Diam.

Photomicrograph of wire
which has been electrolysed.
0.7 % Carbon.

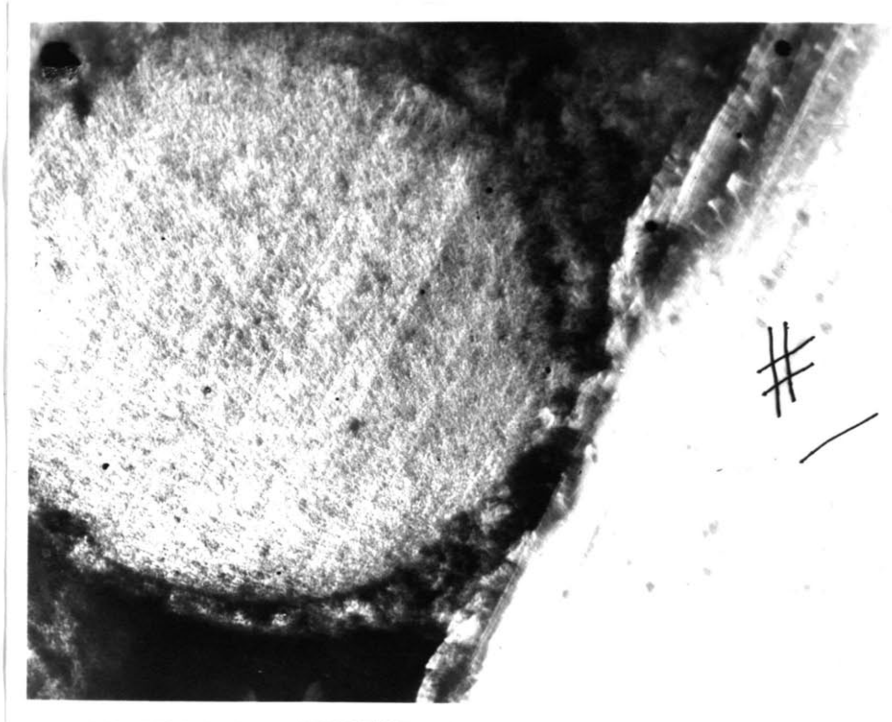
Sketch of the annealing furnace.



The furnace, containing the spring, was started up slowly. When a temperature of 740° C. was reached, the following data were taken.

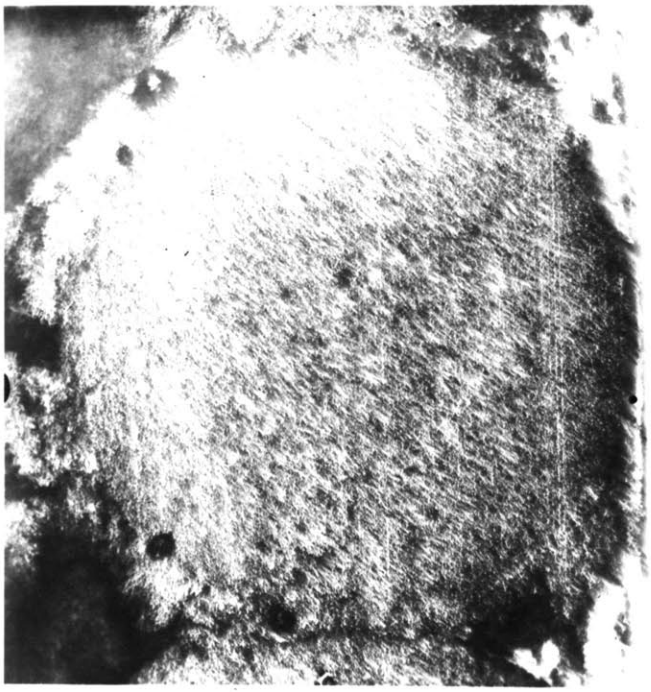
Time	Temperature
11;25 A.M.	740° C.
11:45 "	760 "
12:15 P.M.	500 "
12:45 "	350 "
1:00 "	Room temp.

The spring was covered with a coating of oxide, which when brushed off, left the spring-wire with a diameter of 0.40 mm., instead of 0.46 mm., which was the original size. The slow cooling indicated in the above table removed all strains caused by cold-working and also rendered the wire much less elastic. The temperatures were chosen in accordance with the iron-carbon diagram used in Dr. Fay's lectures on engineering alloys. According to this, the transition-temperature of a 0.7 % carbon steel is about 700° C. Photomicrographs of this wire are shown on the following pages. This wire was electrolysed for one and one-half hours with 3.00 amperes at a temperature of 80-85° C. without its physical properties being affected in the slightest degree.



Magnification 175 Diam.

Photomicrograph of wire
annealed but not electrolysed.
0.7 % Carbon.



P:

#4

Magnification 175 Diam.

Photomicrograph of wire
annealed and electrolysed.
0.7 % Carbon.

The next thing tried was the use of the springs as anodes. This, of course, would never be the case in any plating operation, but it was thought desirable to see what the results would be. A sample of the 0.46 mm. size was used as an anode for fifty minutes with 3.5 amperes, with the temperature at 80-85° C. Its physical properties underwent no change whatever, a slight discoloration of the surface being the only evidence of any change. In all these electrolyses the odor of ammonia was prevalant.

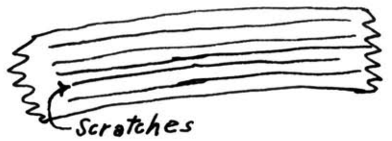
Some of the brass and phosphor-bronze wire, of which samples had been electrolysed before(see page three) were now cold-worked and then electrolysed. The cold-work consisted of hammering to a ribbon between two flat pieces of steel . The ribbon was coiled into a helix, to save space, and placed in the cell. The following are the data.

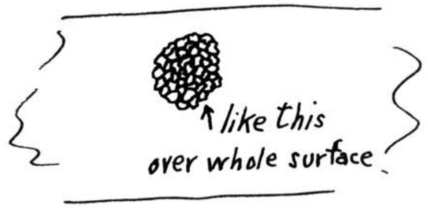
Material	Time	Temp.	Current
Brass	1 h.5 m.	80-85° C.	3.5 amps.
Phosphor-bronze	" "	" "	" "

Neither specimen was affected in the slightest degree, except for a slight surface discoloration.

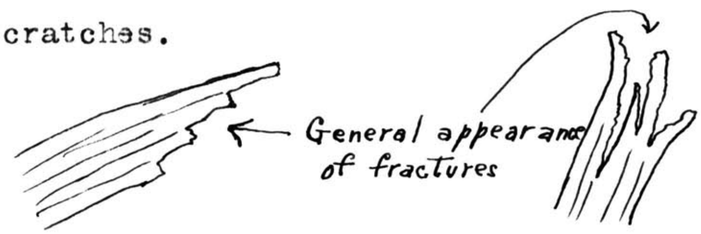
The surfaces of the springs and the fractures were then examined with a microscope. The magnifying power was only about 30-50 diameters, and no photomicrographs could be taken, since the wire was round, and the fractures irregular, so that only part of the object could be brought into focus at one time.

The surface of the wire showed small, shallow scratches running parallel with the axis of the wire for an indefinite length. These were probably caused by the die through which the wire was drawn. The surface also appeared to be composed of small, interlocking crystals, similarin appearto the crystal-structure sometimes developed in etching for photomicrograph work. The surface of the samples of wire which had been electrolysed showed exactly the same scratches and crystals which appeared on the samples which had not been electrolysed . The sketches show how the scratches and crystals occur.

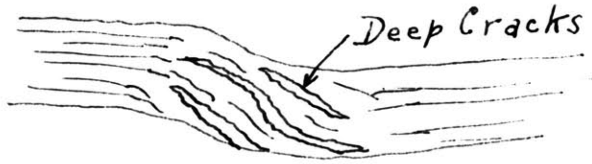




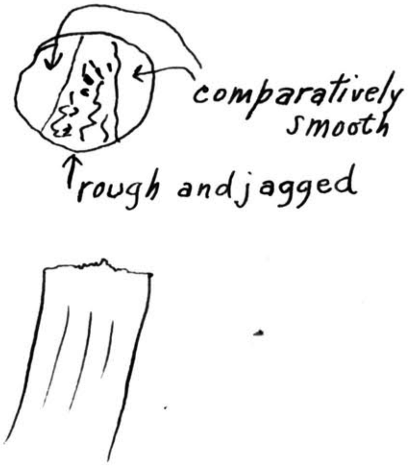
The majority of the fractures seem to follow these scratches.



One sample was twisted, but not far enough to break it. The cracks were very deep, extending nearly to the center of the wire.



Occasionally, however, fractures of a different type occurred. The one on the right is similar to the type called " fracture in detail " in metallography. (see p,17)



Owing to lack of time, the experimental work had to be discontinued with the microscopic examination of the surfaces and fractures. While this examination was going on, however, a sample of the electrolysed spring was boiled in water, as sometimes this treatment renders the brittleness in cold-worked metal less marked. In this case, however, the boiling had no effect, the spring being just as brittle after boiling as before.

SUMMARY OF RESULTS.

The results of the preceeding experiments may be summarized as follows:

1. The rendering of the metal brittle is limited to the use of the wire as a cathode in the electrolysis of, or the electroplating in, a cyanide solution, either simple or complex.

2. The carbon-content and the microstructure remain unchanged.

3. The fractures evidently occur in the surface scratches caused by the die in drawing the wire.

4. The wire need not be coiled into springs in order to have the effect take place.

5. The effect does not take place in annealed wire.

6. Other metals than steel are apparently not affected.

DISCUSSION.

From the limited conditions under which the phenomenon occurs, it is evident that the cyanide radical is a necessary factor in the effect. But since the effect occurs only when the wire is used as a cathode, it was thought that hydrogen deposition would have some effect. But hydrogen deposition has no effect in any other solution. It was also thought that the phenomenon was a case of Cohen's " strain disease " ,but the limited conditions made this seem improbable.

The analytical results show the phenomenon is not a case -hardening effect, which was one idea. The idea of the formation of a brittle hydride of iron was abandoned when the hydrogen-deposition experiment was performed. It may be that a brittle nitride of iron is formed, but this is improbable for two reasons. First, such a compound would probably show up in the microstructure; and second, the nitrogen in the cyanide ions is carried over and de posited on the anode, as cyanogen, whereas the cathode is the place where the effect occurs.

The longitudinal scratches on the surface of the wire may have changed the iron in the scratches to the " amorphous cementing material " of the metallographist. This might render the iron more susceptible to the effect, causing the crack to start in the scratch. However, this is only a guess.

At first it was thought that the strain of coiling the wire into a helix was a factor in the breaking effect, but this idea was abandoned when it was found that coiling was not necessary in order to have the effect take place.

The fact that annealed wire does not show the effect would seem to bear out the idea that it is a case of Cohen's " strain disease ", but this seems to be discounted when the limited conditions are remembered.

In conclusion it must be said that, while it has been found that the phenomenon is not so universal as had been supposed, the explanation is as far off as ever.