furnished in tanks or steel drums, being most advantageously manufactured at the source of production of casing head gasoline. The price of such an article in fairly large quantities bears no relation whatever to the prescription doses of pentane sold for photometric work. It has also been assumed that the most advantageous location for such a plant would be in the neighborhood of a chlorine-caustic soda plant, where the chlorine would be available for use without liquefaction. The diagrams indicate roughly the flow of material.

APPARATUS REQUIRED

1—STORAGE FOR

- (a) Crude pentane, 18,000 gal. steel tank.
- (b) Crude chlorinated product, pentane and chlorpentane, 18,000 gal. lead-lined steel tank.
- (c) Distilled chlorpentane, 8,000 gal. lead-lined tank.
- (d) Sodium acetate, crystalline, 100 ton covered wooden bins.
- (e) Glacial acetic acid, 10,000 gal., 5 wooden tanks, 2,000 gal. each.
- (f) Amyl acetate, finished, 15,000 gal., 3 steel tanks, 5,000 gal. each.

2—CHLORINATION

- 3 units complete, each consisting of one 500 gal. earthenware vessel¹ fitted with lead coil for cold water or brine, glass Hart condenser of the type used for nitric acid, and earthenware receiver for separating recovered pentane and aqueous HCl.

3—STILLS

- 2 Steam jacket Duriron stills, 1000 gal. charge capacity for rectifying chlorpentane.
- 1 Steam jacket copper still for rectifying amyl acetate, acetic acid, and amylene mixture, capacity 900 gal.

4—ACETYLATION

- 3 Copper-lined steel autoclaves, jacketed, heated by hot oil circulation, provided with agitators of copper or Duriron, capacity 900 gal. each.

5—ACCESSORIES

- 1 Centrifugal extractor, 30 in. copper mesh basket, for separating salt from reaction mixture.
- 1 Agitator, copper, for washing amyl acetate with soda ash solution, capacity 900 gal.
- 1 Wooden tank with chain type agitator for washing excess sodium acetate from salt, capacity 500 gal.
- 2 Crystallizing pans, iron, in brick setting, slow direct fire for recovering sodium acetate, 300 gal. each.
- 3 Melting pans, steel in brick setting, slow direct fire for fusing sodium acetate, capacity 200 lbs. sodium acetate each.
- 1 Motor for agitating autoclave, 8 h. p. steam, 200 boiler h. p. for distillation, heating building, pumping, etc.
- 4 Dump cars and track for conveying salt, sodium acetate, etc.
- 1 Motor, 8 h. p., for operating pumps.
- 3 Low-pressure rotary pumps for pumping pentane, amyl acetate, etc.

BUILDINGS

- 1 Shed for storing acetate of soda.
- 1 Building for chlorinating pentane and distillation of chlorpentane, fireproof asbestos board.
- 1 Building for acetylating and distillation of amyl acetate.
- 1 Building for boilers and fusing sodium acetate.

¹ Suitable vessels of this size are regularly manufactured.

ESTIMATED COST OF SYNTHETIC AMYL ACETATE ON THE BASIS OF 600 GALLONS DAILY PRODUCTION

DAILY COSTS	
Gasoline, 990 gal. at 40 cts.	\$ 396.00
Chlorine, 5200 lbs. at 2.5 cts.	130.00
Acetate of soda, 4880 lbs. cryst. acetate at 15 cts.	732.00
Soda ash, 1450 lbs. at 3 cts.	43.50
Interest on \$35,000 at 6 per cent, and depreciation at 20 per cent per annum.	30.30
Labor, one chemist at \$8.00, 10 laborers at \$4.00	48.00
Fuel and Power	40.00
TOTAL DAILY COSTS	\$1419.80
VALUE OF PRODUCTS	
Amyl acetate, 600 gal. at \$4.50 per gal.	\$2700.00
Total daily costs	1419.80
DAILY PROFIT	\$1280.20

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THE EFFECT OF ANNEALING ON THE ELECTRICAL RESISTANCE OF HARDENED CARBON STEELS¹

By I. P. PARKHURST

Received November 24, 1917

The electrical resistance of steels as affected by impurities or by different heat treatments applied over wide ranges of temperature, has attracted the attention of several investigators. A résumé of previous work is here given.

RÉSUMÉ OF PREVIOUS WORK

W. H. Johnson² made a study of the electrical resistance of steels in order to determine the effect of impurities. The resistance of seven samples of different analyses was measured. The impurities were found to increase the resistance, but the data obtained were not sufficient to allow of specific conclusions.

A. Campbell³ determined the effect of stress on the resistance of iron and iron-nickel wires. Practically no change was observed up to the breaking point.

H. Le Chatelier⁴ investigated the effect of high temperatures on the resistance of iron, steel, hard steel, iron-nickel, platinum, etc. His measurements were made in an atmosphere of hydrogen. In a 0.6 per cent carbon steel he observed breaks in the temperature-resistance curves at 710 and 820° C.

H. Le Chatelier⁵ studied the effect of hardening and tempering on the resistance of steels. His results showed that the resistance was increased by hardening and decreased by tempering.

L. Compredon⁶ made a study similar to that of W. H. Johnson, referred to above, and obtained similar results.

J. De War and J. A. Fleming⁷ determined the resistance of iron and nickel at temperatures down to the boiling point of oxygen. They found that the resistance decreased rapidly with the decrease in temperature.

¹ Read in abstract at the Metallurgical Symposium, Boston Meeting, American Chemical Society, September 1917.

² "Chemical Composition and Electrical Resistance of Steel Wire," *J. Iron and Steel Inst.*, **19** (1881), No. 2, 605.

³ "Electrical Properties," *Engineering*, **63** (1887), 468.

⁴ "Electrical Resistance of Iron and Its Alloys at High Temperatures," *Compt. rend.*, **110** (1890), 283.

⁵ "Effect of Tempering on the Electric Resistance of Steel," *Compt. rend.*, **112** (1891), 40.

⁶ "Electro-conductivity of Steel," *Le Genie Civil*, **19** (1891), 309.

⁷ "Electrical Resistance of Iron," *Phil. Mag.*, **34** (1892), 326.

F. Osmond¹ investigated the effects of carbon, silicon, nickel and manganese on the resistance of steels. He found that the resistance was increased by all these elements, and especially by silicon, nickel and manganese. The temperature coefficient fell in a parabolic curve with increase in resistance.

H. Le Chatelier² studied in detail the effects of carbon, silicon, and manganese on the resistance of steels. Carbon was found to increase the resistance of 7 microhms for 1 per cent, silicon 14 microhms for 1 per cent, and manganese 3 microhms for 1 per cent.

C. Benedicks³ investigated the effect of impurities on the resistance of iron and steel. He used commercial iron and steel varying from 0.08 to 1.7 per cent. C. and varying in amounts of silicon, manganese, phosphorus, and sulfur. Calculating the percentages of silicon and manganese to equivalent carbon, he proposed the following formula

$$\rho = 7.6 + 26.8 \Sigma C,$$

in which ρ is the resistance of the steel, 7.6 the resistance of pure iron, and ΣC the sum of the percentages, in terms of carbon, of the impurities in the iron.

M. Portevin⁴ determined the resistance of ternary steels, including alloys with nickel, chromium, tungsten, aluminum, molybdenum, vanadium, titanium, boron and thallium. He discussed also the influence of titanium on the arrest points.

A. P. Schleicher and W. Guertler⁵ studied the resistance of alloys containing 35.25, 30.6 and 25.2 per cent nickel. It was observed that there was a pronounced discontinuity in the resistance at about 420° C. for the steel containing 35.25 per cent nickel, and at 700° C. for the one containing 30.6 per cent nickel. The alloy containing 25.2 per cent nickel gave, in the original condition, abnormally low values, but the resistance increased with each heating until it became stabilized with a discontinuity at 900° C.

A. Portevin⁶ heated steel bars in a salt bath at 750 and 900° C. for varying lengths of time and after quenching, measured the increase in resistance.

K. Honda⁷ investigated the influence of high temperatures on the electrical resistance and magnetic properties of iron, steel, and nickel. He concluded that the magnetic transformation was not an allotropic change, but a gradual change of the property of a phase, due to a change in temperature.

G. K. Burgess and I. N. Kellburg⁸ measured the electrical resistance of pure iron from 0 to 900° C. The resistance increased with a gradually rising rate

¹ "The Electrical Resistance of Iron and Steel," *La Lumière Électrique*, 46 (1893), 93.

² "The Electric Resistance of Steel," *Bulletin de la Société d'Encouragement pour L'Industrie Nationale*, 3, p. 743.

³ "Electric Resistance of Iron and Steel," *Z. phys. Chem.*, 40, [5], (1903).

⁴ "Electric Resistance of Steel," *Revue de Métallurgie, Memoirs*, 6 (1909), 1304.

⁵ "Electric Resistance of Iron-Nickel Alloys," *Z. Elektrochem.*, 20 (1914), 273.

⁶ "Influence of High Temperatures on Magnetic Properties," *Compt. rend.*, 158 (1914), 51.

⁷ "Influence of High Temperatures on Magnetic Properties," *Revue de Métallurgie, Memoirs*, 11 (1914), 383.

⁸ "Electric Resistance of Iron at Varying Temperatures," *J. Wash. Acad. Sci.*, 4 (1914), 436.

to A₂. There was an inflection at A₂ and an abrupt fall in resistance at 894° C. The reverse change took place at approximately the same temperature. The interval was 25° C. The change at A₃ was progressive and thermoelectrically nonreversible. The change at A₂ was reversible.

P. Mahler¹ studied the influence of carbon and manganese on the resistance of steel. The specific resistance increased 7 microhms for 1 per cent of carbon, and 5 microhms for 1 per cent of manganese. Mahler believes that occluded gases increase the resistance, and points out that hydrogen is known to do so.

Edward D. Campbell^{2,3} investigated the effect of annealing on the resistance of quenched steels. He measured the resistance of the quenched steels and subjected them in turn to temperatures of 100, 200, 300° C., etc. The annealing at 100° C. was prolonged for 48 hrs. The time of annealing at the other temperatures was from 1 to 2 hrs. He plotted curves showing the resistance against the temperature of annealing.

OBJECT OF THE PRESENT INVESTIGATION

The object of the investigation here presented was to determine the rate of softening of quenched steels, under conditions in which the temperature of annealing is kept constant. Changes in the electrical resistance were used as a measure of the changes in hardness.

FIG. 1—APPARATUS FOR QUENCHING COILS

The work was carried out by first quenching the steel and measuring the resistance. This was followed by annealing the steel for a definite time at a definite temperature, and again measuring the resistance. This procedure was repeated at the same temperature but with an increasing interval of time, followed by another measurement of the resistance. The total period of annealing for the different specimens varied from 90 to 190 hrs. The results were then plotted as time against resistance.

EXPERIMENTAL

The steels were treated in the form of a wire coil. The specimens were prepared by forging steel bars

¹ "Electric Resistance of Steel," *Revue de Métallurgie*, 12 (1915), 345.

² "The Influence of Heat Treatment on the Thermoelectric Properties and Specific Resistance of Carbon Steels," *J. Iron and Steel Inst.*, [2], 94 (1916), 286.

³ "Do Equiatomic Solutions of Iron Possess Equal Resistances?" *Trans. Faraday Soc.*, 12 (1917), 1.

down to $\frac{1}{8}$ in. round. The pieces of this size, about 4 in. long, were drawn down to wires varying from 0.014 to 0.019 in. in diameter (0.355 to 0.482 mm.). From 20 to 50 cm. of this wire were used as a specimen. The specimens were heated and quenched in a vacuum, being contained in a silica tube which was heated in an electric combustion furnace. Temperatures were measured with a platinum-platinum-rhodium thermocouple.

The arrangement for heating and quenching is shown in Fig. I. The specimen was placed in the glass extension of the silica tube. The tube was then placed in the tube furnace and kept there for 5 min. At the end of this time it was evacuated, withdrawn from the furnace, inverted, and replaced in the furnace. After about 1 min. it was again withdrawn and the specimen quenched. The object of this procedure was to bring the coil to the desired temperature as quickly as possible, in order to prevent oxidation. It was necessary to guard carefully against oxidation, since the coils were long and slender. It will be shown later that the effect of oxidation was small.

After measuring the resistance, the method of which will be explained later, the coil was annealed at a definite temperature. The temperatures chosen were 125, 150, 175 and 250° C. For the first three temperatures the specimens were annealed in a constant temperature paraffin bath, which was heated on an electric hot plate to a temperature which was a few degrees below that desired. The temperature was then further raised and adjusted by means of a resistance coil in the bath. The current in the coil was regulated through a thermostat regulator and a relay. The temperature was constant to about one degree.

For the first 5 min. the specimen was immersed directly in the paraffin. For longer annealing the specimen was placed in a tube immersed in the paraffin. The reason for putting the coil directly in the paraffin was to allow a closer determination of the time of annealing. The specimen would take up the temperature of the liquid much more quickly than that of air, hence the time of annealing could be more accurately measured in the paraffin than in air. For longer annealing, a small difference in time would make much less difference in the results, hence the tube was used. This was desirable whenever possible in order to prevent any chance of carbonization.

For annealing at 250° C. a constant temperature oven was used, in which the temperature varied about 5° C.

For measuring the resistance of the specimens, they were immersed in a tube of alcohol, which was placed in a thermostat regulated to 30° C. The maximum variation of the temperature was 0.05° C.

The resistance was measured with a Kohlrausch bridge used as shown in the diagram in Fig. II. The unknown resistance X and a known resistance, R , are connected in series, and in parallel with them is the slide wire of the bridge. The bridge is balanced with each end of each resistance, thus making four readings. If the readings for the known resistance

are a and b , and those for the unknown resistance c and d , then

$$\frac{X}{R} = \frac{d - c}{b - a}$$

This method was used in order to eliminate the effect of contact resistance. The double-throw switch was used in order to eliminate the effects of all thermo-electromotive forces and generated electromotive forces.

FIG. II—APPARATUS FOR MEASURING RESISTANCE

The resistance measurements themselves were accurate to one part in one thousand. However, the impossibility of placing the contacts at exactly the same point each time increased the error. This added error depended on the length of the coil. For both contacts it was not more than 0.5 mm. This would give a possible error of 0.25 per cent for coil No. 5, which was the shortest, and 0.1 per cent for the longer coils. This makes a total probable error of from 0.2 to 0.35 per cent.

The analyses of the specimens and the dimensions of the coils are given in the following tables:

No.	ANALYSES OF SPECIMENS						DIMENSIONS OF COILS	
	C	Si	P	Mn	S		Diameter	Length
	Per cent	Per cent	Per cent	Per cent	Per cent		Mm.	Mm.
1.....	0.05	0.006	0.021	0.055	0.025		0.355	514
2.....	0.09	0.059	0.013	0.044	0.019		0.368	500
3.....	0.18	0.025	0.090	0.068	0.092		0.482	486
4.....	0.25	0.058	0.109	0.075	0.036		0.431	503
5.....	0.45	0.122	0.112	0.092	0.106		0.431	196

The results of the resistance measurements are plotted in the following curves, which show the effect of the duration of annealing on the resistance of the steels.

FIG. III

CONCLUSIONS

The total change in resistance increases with the carbon content of the steel. The change is very rapid at the beginning of the annealing and becomes slower as the resistance decreases. However, there was no indication in any case that the change was complete at the end of the test.

Since the resistance of a steel changes with the hardness, the curves are a fair indication of the varying rates at which hardened steels are softened by annealing at a constant temperature. The larger part of the change is completed within a few minutes, but the change is not entirely complete in 113 hrs.

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VOLUMETRIC DETERMINATION OF FREE SULFUR IN
SOFT RUBBER COMPOUNDS

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The published and accepted methods of determining free sulfur in a rubber compound are more or less tedious, and, where manufacturing operations are dependent upon them, are the cause many times of serious delays. These delays, the cost of materials required, and the time consumed by the determining process, make these methods expensive. It was with this in mind that the following method was evolved and results obtained both in conservation of time and materials and also in accuracy lead us to believe it may be of interest to others who are using the present-day accepted methods.

METHOD

The proposed method depends on the fact that sulfur when heated with an alcoholic potash solution is converted into a mixture of potassium sulfide and potassium thiosulfate, both of which may be titrated with standard iodine by usual methods as given in this article. The free sulfur is determined in the acetone extract from the rubber compound. The resinous extract of certain commercial rubbers and the extract of other compounding materials are acted upon by

the alcoholic potash solution and by various standard solutions used in analysis, thereby rendering necessary the application of corrections. The amount of correction or blank used in titrating is determined by the nature and amount of the various ingredients in the extract from the rubber compound. This limits the use of the method with confidence to a sample of rubber, the composition of which is known to the analyst. The proposed method can be used successfully where a large number of tests are being run on a compound made up to a certain formula, for example, insulated wire compounds, boot and shoe compounds, etc.

The equation generally given for the oxidation of sulfur by a water solution of potassium hydroxide is:

This varies with change of conditions. When using an alcoholic potash solution instead of potash in water more thiosulfate is formed than is indicated in the equation and in some cases the conversion to this product is complete. Using this principle, a method has been worked out which is as follows:

PROCEDURE

Extract a 2-g. sample of rubber compound with acetone into a 300 cc. Erlenmeyer flask until the free sulfur has been removed. A similar compound, which is known to be free of free sulfur, is tested at the same time. This is used to determine the blanks in the subsequent titrations.

Evaporate the acetone gently until little remains, completing the drying in an oven at 100° C. This operation need not take longer than a half hour. The sulfur in the dried extract is oxidized to thiosulfate and sulfide with 25 to 50 cc. of 5 per cent alcoholic potash solution by boiling gently for one hour, using a small glass funnel placed in the neck of the flask for a condenser. Remove from heat. Wash and remove funnel from flask. Add 25 to 50 cc. of ammonium zinc chloride solution¹ and just bring to boiling.

¹ This solution is made as follows: 10 g. of zinc oxide are dissolved in dilute hydrochloric acid. The solution is made alkaline with ammonia (sp. gr. 0.90), adding 50 cc. in excess. The solution is now made up to a liter.