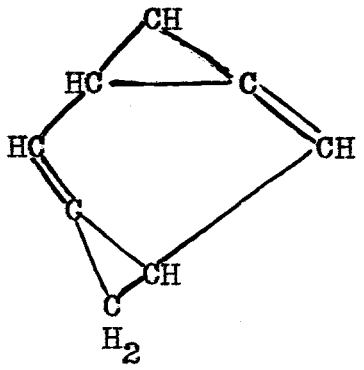
4. By treatment of C_8H_8 with hypochlorite there is produced terephthalic aldehyde which must be derived from a compound having the basic structure -



Recent Advances in Carbonylation Chemistry

The latest development in the carbonylation chemistry is the use of the metallic hydro-carbonyls which are strong acids and react quite differently than do the above simple carbonyls. Dr. Reppe has worked with both the nickel and cobalt hydrocarbonyls.

Dr. Reppe developed new methods of preparing the compounds, H Co $(CO)_4$ and $H_2Fe(CO)_4$, in large quantities and studied their physical constants and chemical behavior. This work showed that H $Co(CO)_4$ belonged to the group of strongest acids (about like HCl) and that H_2 $Fe(CO)_4$ behaved like an average mono-basic acid. These compounds were reacted with acetylene and olefine in the presence of water and the reaction-products in the case of the olefines proved to be aliphatic alcohols, and in the case of the acetylene to be hydroquinone, or the like. The empirical equation for the reaction with the iron compound can be the following:

$$H_2Fe(CO)_4 + 2\ H_2C = CH_2 + 2\ H_2O \longrightarrow$$

$$2\ CH_3CH_2CH_2OH + Fe(HCO_3)_2$$

that is, $2\ C_2H_4 + 3\ CO + 2\ H_2O \rightarrow CH_3(CH_2)_2OH + 2\ CO_2$

The reaction progresses at about 100-110°C. and needs no Iodine, but there should be present an organic base that does not react with CO (amines), to form the

$H_2Fe(CO)_4$, as follows:

$$2\ Fe(CO)_5 + base + 2\ H_2O \longrightarrow$$

$$2\ H_2Fe(CO)_4 + base + 2CO_2$$

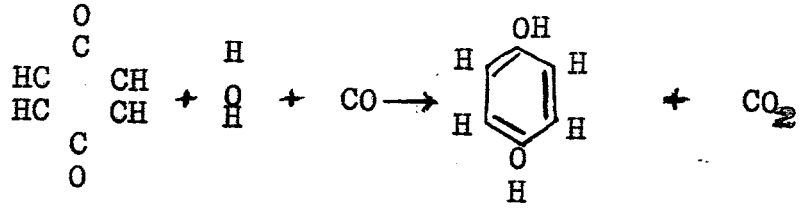
In contrast to $Ni(CO)_4$, the iron hydrocarbonyl can react at ordinary pressure but has the disadvantage that for each CO taken up to form product, two CO_2 molecules are lost. The relation between this reaction and that with $Ni(CO)_4$ as catalyst in the reaction between ethylene, carbon monoxide, and water to give either propionic acid or its anhydride is recognizable.

If a portion of the water in the above empirical equation is substituted by NH_3, propylamine is produced, as well as the di- and tri- propylamine.

$$CH_2 = CH_2 + 3CO + H_2O + NH_3 \longrightarrow$$

$$H_2N - CH_2 - CH_2 - CH_3 + 2CO_2 .$$

By extension of this olefinic reaction with metallic hydrocarbonyls, Dr. Reppe thought to arrive at unsaturated alcohols but, instead, with substituted acetylene arrived at hydroquinone derivatives in a yield of about 30% as far as his investigations have been conducted: empirically it seems to progress about as follows:



Stoichiometrically, the reagents react in the following ratio:

$$H_2Fe(CO)_4 + 4C_2H_2 + 2H_2O \longrightarrow$$

$$2\ C_6H_6O_2 + Fe(OH)_2$$

When/employed substituted acetylenes and $H_2Fe(CO)_4$, benzene derivatives are formed; for example $CH_3 - C \equiv CH$

665

yields trimethylbenzene.

The success of this new carbon-monoxide chemistry is attributable to this first use of these hitherto unusable catalysts or their substitution products, i.e. metal carbonyls or metal hydrocarbonyls, as is also the similar situation in the use of the heavy metal acetylides and their first employment as catalysts in the ethylenation reactions.

(The metallic hydrocarbonyls are not new chemical compounds. They have been extensively investigated by W. Hieber and his colleagues. In 1932, he and others published method of preparation and certain reactions of $Fe(CO_4)H_2$ in the Z. anorg. allgem. chemie, Vol. 204, pages 145-64. Hieber therein describes the preparation of $Fe(CO)_4\ H_2$ according to the following reaction:

$$Fe(CO)_5 + CH_3ONa + H_2O \longrightarrow$$

$$Fe(CO)_4\ H_2 + CH_3OCO_2Na$$

Hieber also states that alkaline solutions of iron hydrocarbonyl have a strongly reducing action on organic substances such as nitrobenzene, quinone and dyes - for example indigo. Although stable in alkaline solution, the hydrocarbonyl easily decomposes in the free state or in the presence of acids because of the initial reaction $2\ Fe(CO)_4H_2 \longrightarrow Fe(CO)_5 + Fe(CO)_3 + H_2$ which proceeds further leading to indefinite results).

665

APPENDIX A.

A LIST OF IMPORTANT PATENTS, BOTH GERMAN AND FOREIGN ISSUED ON INVENTIONS OF DR. REPPE

DRP 489 537
DRP 550 425
DRP 584 840
DRP 591 845
DRP 618 120
DRP 625 660
DRP 624 886
DRP 647 036
DRP 664 231
DRP 695 219
DRP 698 273
DRP 701 825
DRP 705 273
DRP 709 370
DRP 714 490
DRP 724 759
DRP 727 476
DRP 624 845
AP 1827 285
EP 504 957
EP 512 182
FP 842 577
FP 853 148
PP 865 428

DRP 510 712
DRP 552 987
DRP 588 352
DRP 593 399
DRP 621 963
DRP 631 016
DRP 643 220
DRP 662 156
DRP 679 607
DRP 696 774
DRP 699 430
DRP 703 956
DRP 706 108
DRP 711 709
DRP 715 268
DRP 725 326
DRP 728 466

AP 1998 413
EP 508 543
FP 50208/Zspat.
FP 844 533
FP 853 606
Schweiz. 220 204

DRP 511 517
DRP 566 033
DRP 589 970
DRP 610 371
DRP 624 622
DRP 636 077
DRP 645 112
DRP 662 936
DRP 684 820
DRP 696 779
DRP 699 945
DRP 704 235
DRP 706 694
DRP 713 565
DRP 715 815
DRP 725 532
DRP 730 648

EP 466 316
EP 510 876
FP 806 715
FP 845 600
FP 858 185

DRP 550 403
DRP 578 994
DRP 591 774
DRP 617 543
DRP 625 017
DRP 639 843
DRP 646 995
DRP 663 779
DRP 695 218
DRP 697 802
DRP 700 036
DRP 704 237
DRP 708 262
DRP 714 359
DRP 721 004
DRP 726 714
DRP 734 241

EP 497 939
EP 510 902
FP 814 349
FP 851 178
FP 865 354
Schweiz P 220 208

665

DOCUMENTS

Three type-written and bound documents relating to the herein-discussed subject-matters have been deposited with the MIRS in CIOS Document Bag No.3518 for safe-keeping. They have been duplicated in the B Series of microfilms which will be filed in Washington, D.C., in the custody of the Petroleum Administrator for War. The documents consist of:-

TOM-69

(1) Report on Cyclopolyolefines;
33 Pages and Appendix 24 Pages.

(2) Dr.J.W.Reppe: Personal History and Contributions in the Field of Acetylene Chemistry;
39 Pages and 2 Tables.

(3) Dr.J.W.Reppe; Further Details of his Work including Activities in Divers Fields of Organic Chemistry; 10 Pages.

B.) BLAST FURNACE LININGS

While at the MANNESMANNROHREN plant at DUISBURG-HUCKINGEN in connection with electric steel furnaces, the technical organization were also questioned about the performance of their carbon-lined blast furnaces. These linings are of the pre-baked, large machined block (single pieces up to about 23"x29"x80") type. The general results with this type of lining have been so satisfactory that MANNESMANNROHREN have completely standardized on them.

At the time of the shut-down at the end of the war, the following campaign figures had already been realized for these carbon-lined furnaces. It is believed that even Furnace No. 1 is capable of being restarted.

Blast Furnace Number	Date Lining Installed	Long Tons Produced to April, 1945	No. of Run-Outs
1	May 1929	3,150,000	1
2	May 1929	2,480,000	3
3	June 1937	1,400,000	0
4	May 1939	1,000,000	0

The run-outs were at the iron notch and were caused by failures not connected with the carbon linings.

710

PART V

SUMMARY OF PLANTS

A.) ELECTRODE MANUFACTURERS

Firm: C. CONRADTY
Location: NÜRNBERG 2 - RÖTHENBACH
Target Number: 1/121
Plant Condition: Only slightly damaged; laboratory building burned down; one graphitizing transformer in need of repairs.
Personnel Interviewed: EUGEN CONRADTY, OTTMAR CONRADTY, MR. ZÖLLNER, MR. KRETSCHMAR
Date Visited: August 25-27, 1945
Research and Development: This firm has no separately organized and equipped research and development facilities, all of its experimental work being done in its regular production departments by the regular operating staff.
General Comments:

This is a very old plant founded in 1855. The graphite electrode department was installed in about 1942-3 and is well-equipped with modern machinery.

This company also owns a graphitizing plant in AFFOLTERN, SWITZERLAND. The basic stock for processing by the Swiss plant was supplied from the NÜRNBERG plant.

Firm: C. CONRADTY
Location: KOLBERMOOR (near ROSENHEIM)
Plant Condition: Undamaged
Personnel Interviewed: MR. J. HECKEL
Date Visited: August 21, 1945
General Comments:

This is a small branch factory of the NÜRNBERG company, and is equipped only for graphitizing the basic stock supplied from NÜRNBERG. The original small graphitizing unit is not in good operating condition, but the two relatively new, medium size units are in good condition.

710

Firm: I.G.F.
Location: GRIESHEIM (near Höchst am Main)
Target Number: 8/59a
Plant Condition: Only slightly damaged
Personnel Interviewed: DRS. ENGELBRETZ, PETER
Date Visited: August 17, 1945
Research and Development: This plant has no facilities for research and development on carbon products, except as can be carried out with operating facilities and organization.
General Comments:

This plant is equipped only for the manufacture of basic baked stock for either carbon or graphite electrodes. Graphitizing was formerly done by their BITTERFELD plant, but now would have to be performed by either the SIEMENS or CONRADTY plants.

Firm: SIEMENS PLANIAWERKE
Location: BERLIN-LICHTENBERG
Target Number: C31/110
Plant Condition: Reportedly only the brush department was damaged, but the entire plant equipment is now boxed for shipment to RUSSIA.
Personnel Interviewed: DRS. ADAM, RAGOSS, CONRATH, WARTBURG, OBERING, RHEE
Date Visited: September 20, 1945
Research and Development: This plant was well organized for research and development, and was the leader in this industry in GERMANY.
General Comments:

This plant produced the basic baked stock for graphitization at the MEITINGEN branch plant.

Firm: SIEMENS PLANIAWERKE
Location: MEITINGEN (near AUGSBURG)
Plant Condition: Undamaged
Personnel Interviewed: DR. H. MENSCHING, ING. H. HUBMANN
Date Visited: August 22-23, 1945
General Comments:

This is a branch factory of the BERLIN company, and is equipped only for graphitizing. The basic baked stock was originally furnished from the BERLIN factory. In order to use the graphitizing capacity of this plant,

710

the basic stock would have to be supplied from some other plant, such as the I.G.F. plant at GRIESHEIM.

This is the largest and most efficient graphitizing plant in GERMANY.

Firm: AUGUST THYSSEN HÜTTE
Location: HAMBORN
Target Number: C31/478
Plant Condition: Badly damaged
Personnel Interviewed: DR. BRANDI
Date Visited: September 1, 1945
General Comments:
Reviewed their experiences with electric steel furnaces. Electrode usage about 8-10 kg. per ton with cold charges.

Firm: BOCHUMER VEREIN
Location: BOCHUM
Plant Condition: Damaged
Personnel Interviewed: DIR. BREMER
Date Visited: August 30, 1945
General Comments:
Discussed their experiences with 40 ton electric steel furnaces with 20" graphite electrodes. Usage about 8½ kg. per ton.

Firm: DEMAG ELEKTROSTAHL
Location: DUISBURG, Fuldastrasse 4
Target Number: C31/89
Plant Condition: Not inspected
Personnel Interviewed: ING. GENVO
Date Visited: September 3, 1945
General Comments:
Discussed general design features and trends in electric furnaces.

Firm: DEUTSCHE EDELSTAHLWERKE
Location: KREFELD
Plant Condition: Slightly damaged
Personnel Interviewed: DR. MARTIN, ING. VOIGT
Date Visited: September 3, 1945

710

General Comments:
Reviewed their experiences with electric steel furnaces. Graphite electrode usage about 10 kg. per ton; carbon electrode usage about 13 to 16 kg. per ton.

Firm: FRIED. KRUPP
Location: ESSEN-BORBECK
Target Number: C31/284
Plant Condition: Badly damaged
Personnel Interviewed: DIR. HEISCHKEIL
Date Visited: August 31, 1945
General Comments:
Reviewed their experiences with electric steel furnaces of 50 ton capacity. Graphite electrode usage about 8.5 to 9.5 kg. per ton.

Firm: LUDWIG RIEDHAMMER
Location: NÜRNBERG, Burgschmiedstrasse 42
Plant Condition: Office damaged
Personnel Interviewed: ING. RIEDHAMMER
Date Visited: August 26, 1945
General Comments:
This man is a consulting engineer, specializing in the design of furnaces, kilns, etc. for the carbon and ceramic industries. He has designed and supervised the installation of carbon electrode plants in JAPAN, RUSSIA, ITALY, FRANCE, etc.

Firm: MANNESMANNROHREN
Location: DUISBURG-HUCKINGEN
Plant Condition: Slightly damaged
Personnel Interviewed: DR. KNAPP, ING. KAHLHÖFER
Date Visited: September 1, 1945
General Comments:
Discussed their experiences with electric steel furnaces and carbon linings for blast furnaces.

710