PATENT SPECIFICATION

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International Classification:—**B01j. C07c.**

COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German company, of Oberhausen-Holten, Germany, and LURGI GESELLSCHAFT FUER WAERMETECHNIK M.B.H., a German company, of Frankfurt a.M., Heddernheim, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the hydrogenation of carbon monoxide.

In the production of precipitated iron, cobalt and nickel catalysts it has long been known to add promoters to increase the activity of the catalysts. Although the definition of the term promoter is frequently not very precise and although such promoters or some of them also function to a certain extent as supporting materials for the catalysts proper, certain elements and/or their compounds are definitely effective as catalyst promoters. Among the most important of these are the alkali-metals which, particularly in iron catalysts, are nearly always present in a smaller or larger amount and in various forms such, for example, as carbonate, silicate, phosphate, fluoride, and the like. Moreover, copper and silver are frequently mentioned as promoters. Further promoters, although more rarely used, are, for example, alumina, cerium, vanadium, chromium, manganese and zinc.

The most important of the class of compounds which are known partly as promoters and partly as supporting materials are magnesium, calcium, strontium and barium compounds, for example, calcium carbonate, magnesium carbonate, dolomite and the like. The large quantities which are frequently used of these compounds clearly reveal that they are present as supporting materials rather than as promoters. It has been disclosed in the literature, however, that calcium in an amount of about 10% based on the iron present exhibits a favourable promoting effect on the activity of the catalyst. Catalysts composed of or containing iron and copper in a proportion of about 10:20 to 10:40 are already known.

It has very surprisingly been found that barium produces a particularly advantageous effect in the hydrogenation of carbon monoxide as compared with magnesium, calcium and strontium, and that synthesis products containing more than 50% of oxygen-containing organic compounds can be obtained with an iron-copper-barium-alkali catalyst.

According to the invention, a process for the hydrogenation of carbon monoxide comprises passing a synthesis gas containing $CO:H_2$ in the ratio of from 1:0.5 to 1:10 at a temperature in the range 150°—300° C. and at a pressure of not less than 10 atmospheres over a reduced catalyst which contains iron, copper, barium and an alkali metal compound, the iron, copper and barium having been co-precipitated from a common solution of salts of the three metals, the barium oxide content of the catalyst being from 10—50 parts, the copper content being more than 25 parts and the alkali-metal content (calculated as K_2O) being more than 2 parts per 100 parts of iron, and more than 50% of the iron in the catalyst being in the metallic state.

The $CO:H_2$ ratio in the synthesis gas is preferably from 1:1 to 1:2 and the preferred conditions of temperature and pressure are within the ranges 180°—250° C. and 30—50 atmospheres respectively.

The catalyst preferably contains from 10 to 30 parts of barium oxide, from 50 to 200 parts of copper, and more than 5 parts of alkali (calculated as K_2O), all per 100 parts by weight of the total iron in the catalyst. It is advantageous for more than 75% of the iron in the catalyst to be in the elementary or metallic state. The catalyst preferably contains little or no supporting material but where supporting material is used it should advantageously not be present to the extent of more than 10% by weight of the total iron in the catalyst.

The effect attained by the process in accordance with the invention consists not only in an increase in the yield of oxygen-containing organic compounds as compared with the yield

[*Price 3s. 6d.*]

obtained with catalysts containing other alkaline earths, but also in the advantageous mechanical properties of the catalysts. These mechanical properties are of great importance in a synthesis process which results in a considerable formation of oxygen-containing organic compounds since the synthesis product contains, in addition to alcohols, esters, ketones, aldehydes and the like, appreciable quantities of free acids which attack the catalyst particles so that with unstable particles, disintegration of the particles in the synthesis reactors accompanied by high pressure drops and obstruction of the tubes must be expected.

Although the advantageous results obtained by the process according to the invention are partly brought about by the combination of iron-barium alone, particularly as far as the mechanical stability of the catalyst particles is concerned, the optimum yields of oxygen-containing compounds and the most favourable catalyst activity are only obtained if copper and alkali, in addition to iron and barium, are also present in the catalyst in the quantities referred to above.

The alkali-metal is incorporated in the catalyst (impregnation) in the form of the hydroxide, carbonate, bicarbonate or of volatile or decomposable organic compounds, for example, formates and oxalates. The use of phosphates is also possible. Less suitable compounds include, for example, silicates and borates.

The production of the catalysts in accordance with the invention is generally effected in the conventional manner by rapidly precipitating the iron copper and barium from an aqueous solution of their salts with alkali at the boil. Catalysts having particularly good properties have been found to be obtained if the *p*H value of the aqueous suspension upon termination of the precipitation is above 7 and preferably above 8.2 However, a *p*H value in excess of about 10 is not favourable. It is essential, in order to obtain a catalyst of optimum activity that the barium be present in the solution of the metal salts and be precipitated from the solution with the iron and copper. Methods of operation are also known for the production of catalysts in which the alkaline earths are stirred in after termination of the precipitation in a manner which, for example, is analogous to that used for the introduction of kieselguhr. In this case, the alkaline earth compound functions more or less as a catalyst-supporting material and does not exhibit the advantageous properties as in the catalyst according to the invention. These properties are only present if barium is precipitated from solution simultaneously with the other components.

After the precipitation the catalyst mass is filtered hot. It is then possible, by a partial wash, to adjust the alkali content to the desired amount. It is also possible, however, first to effect a total wash which is suitably carried out with condensate water but which may under certain circumstances also be effected with tap water, and subsequently to incorporate the desired alkali-metal compound in the catalyst mass by impregnation. Thereafter, the catalyst mass is moulded, for example, in an extrusion press. Prior to moulding, it may be advantageous in certain circumstances to dry the catalyst mass for a short period to reduce its water content. A water content of between about 50% and 70% has been found to be the most advantageous for moulding the mass in an extrusion press. The moulded particles are subjected to a final drying at a temperature of about 100° C., crushed and sieved. However, it is also possible, for example, to brush or otherwise form the catalyst mass into thin layers on metal plates, to dry it at a temperature of about 100° C. to a water content of about 5—10%, and to crush and to sieve the dried mass. The particle size of the catalyst is determined within certain limits by the depth of the layer of the catalyst to be used in the synthesis. If the layer depth is only low, pellets of, for example, as small as 0.5 mm. may be used with good results. With deep layers of, for example, between 5 and 10 metres, the catalyst pellets will preferably have a size of between about 1.5 mm. and 3 mm. Small-sized catalyst pellets have the advantage of exhibiting a particularly high activity.

The reduction of the catalyst according to the invention may be effected at normal pressure, under partial vacuum and frequently advantageously at superatmospheric pressure as, for example, the pressure to be used later in the synthesis. It is possible at normal pressure to operate with high gas flow velocities of between about 50 and 200 cm./second, calculated under standard conditions. When the reduction is effected under pressure, an effective gas flow velocity of between about 5 and 30 cm./second is preferred. The reduction may be effected with gases containing hydrogen and/or carbon monoxide. The temperature used in the reduction lies between about 150° C. and 350° C. and is preferably between 250° C. and 300° C. The reducing gases should have as low a water content as possible, advantageously below 1 gram per cubic metre and preferably less than 0.1 gram/cubic metre of reducing gas. In any case, it is advantageous to charge the catalyst to the reduction step with as low a water content as possible, that is, with a water content of below 2% and preferably of below 0.5%. This low water content is obtained by drying at temperatures of between 100° C. and 200° C. which drying is suitably effected in a current of air.

It has furthermore been found to be advantageous for more than 75% of the iron in the catalyst to be in the metallic state. Catalysts of this type give the highest yields of oxygen-containing organic compounds whilst the reaction temperatures are at the same time low.

The synthesis pressure is at least 10 atmospheres and is preferably between 30 and 50 atmospheres. High yields of oxygenated compounds may be obtained with a long useful catalyst life and a relatively low formation of C_1 and C_2 compounds.

Gases of various composition the $CO:H_2$ ratio of which ranges between about 1:0.5 and 1:10 may be used for the synthesis. In general, a ratio of between 1:1 and 1:2 is preferred. The use of a synthesis gas in which the $CO:H_2$ ratio is within the range 1:0.5 to 1:1 results in an increased yield of high molecular weight oxygen-containing organic compounds, predominantly in the form of esters, whilst with an increase in the hydrogen content of the synthesis gas so that the $CO:H_2$ ratio is less than ½ an increased yield of alcohols is obtained.

The use of gas recycling in the method of operation according to the invention is generally preferred with a recycle ratio (recycled gas: fresh gas) of 1:1 to 3:1. It is also possible, however, to operate these catalysts in a synthesis with a single pass of the gas, that is to say, with once-through operation. High yields and high $CO+H_2$ conversion rates may be obtained with the catalysts in accordance with the invention even with single-stage operation. However, a two-stage or multi-stage operation with the insertion, if necessary or desired, of CO_2 scrubbing units between the individual stages is frequently advantageous.

Particularly favourable operation is possible with the catalysts described above if a fairly high gas load or space velocity of, for example, 200—500 volumes of gas per volume of catalyst per hour is used. In this case, a considerable increase in the yield of alcohols boiling in the range of between about 200° C. and 300° C. as compared with a normal gas load of 100 v/v/hr. is observed.

The superior effect of barium oxide in the production of oxygen-containing organic compounds over the effect of calcium oxide are strontium oxide, is shown in the results set forth in Tables 1 and 2. The barium-containing catalyst employed in the run, the results of which are given in Table 1 was prepared by precipitation from a boiling solution which contained, per litre, 40 grams of iron, 8 grams of copper and 40 grams of BaO in the form of the nitrates, by adding the solution of the nitrates to a boiling solution of sodium carbonate containing about 105 grams Na_2CO_3/litre of solution. The precipitate was subsequently washed very carefully with hot condensate water and thereafter impregnated with potassium carbonate so that 8 parts of alkali, calculated as K_2O, were present per 100 parts of iron. The catalyst mass was brushed on to metal plates, dried for 24 hours at a temperature of about 110° C. and subsequently crushed to a grain size of 2—4 mm. In the same manner, two other catalysts were produced, one containing 40 grams of CaO in place of the 40 grams BaO and the other containing 40 grams of SrO in place of the 40 grams of BaO. These catalysts were reduced for 4 hours at a temperature of 320° C. at normal pressure with a gas mixture consisting of 75% H_2 and 25% N_2 using a linear gas velocity of 1.5 metres/second. The reduction value of all catalysts ranged between 90 and 95%. The following table shows the synthesis results obtained with these catalysts under the following conditions:—

Synthesis pressure	30 atmospheres
Synthesis gas	Water gas
Gas load of the catalyst	100 volumes of gas per volume of catalyst per hour

The synthesis reactors used were the so-called double-tube reactors.

TABLE I.

Catalyst composition	8 K_2O 100 Fe 20 Cu 100 BaO	8 K_2O 100 Fe 20 Cu 100 CaO	8 K_2O 100 Fe 20 Cu 100 SrO
Synthesis temperature ° C.	195	210	224
$CO+H_2$ conversion %	61	55	45
Products boiling above 320° C. based on total liquid product %	18	13	11
Olefins 30°—180° C. %	17	18	22
Oxygen-containing organic compounds 80°—180° C. %*	62	56	56
Olefins 180°—320° C. %	18	19	30
Oxygen-containing organic compounds 180°—320° C. %	67	56	36
Above 320° C. %	54	44	37
Above 460° C. %	38	32	40

In another series of experiments in which only 50 instead of 100 parts of alkaline earth were used, similar results were obtained.

TABLE 2.

Catalyst composition	8 K_2O 100 Fe 1 Cu 100 BaO	8 K_2O 100 Fe 1 Cu 100 CaO	8 K_2O 100 Fe 1 Cu 100 SrO
Synthesis temperature ° C.	210	232	240
$CO+H_2$ conversion %	55	48	41
Products boiling above 320° C. based on total liquid product %	16	8	7
Olefins 30°—180° C. %	13	27	22
Oxygen-containing organic compounds 80°—180° C. %*	63	51	58
Olefins 180°—320° C. %	12	25	22
Oxygen-containing organic compounds 180—320° C. %	55	40	48
320—460° C. %	48	32	40
Above 460° C. %	32	16	—

*The oxygen-containing organic compounds boiling below 80° C. are for the predominant part contained in the aqueous phase.

In another series of experiments in which continuous operation was used, similar results were obtained.

In the accompanying drawings, the effect of the barium and copper content on the activity of the catalyst is shown.

In each of Figures 1 to 4 of the drawings, the Cu contents of the catalysts in parts by weight per 100 parts of iron are given as abscissæ, and the synthesis temperatures in degrees Centigrade are given as ordinates. Each of the catalysts had been impregnated with 8 parts of K_2O per 100 parts of Fe, as described in relation to the catalysts employed in the runs the results of which are given in Tables 1 and 2. The synthesis pressure in each case was 30 atmospheres and water gas was used as the synthetic gas. The $CO+H_2$ conversion in each case was maintained in the range 61—63%.

The results shown in Figure 1 were obtained with a normal gas load or space velocity of 100 volumes of synthesis gas per volume of catalyst per hour (100 v/v/hr.). Figure 1 shows that with an increasing copper content at normal gas load a considerable improvement of the activity and a decrease of the synthesis temperature is made possible, and that a reduction of the barium oxide content from 100 to 25 parts based on 100 parts of iron permits a certain decrease of the synthesis temperature.

The results shown in Figure 2 were obtained with double the normal gas load, that is to say, at 200 v/v/hr. Within the temperature range provided, at least 5 parts of copper are required with a ratio of 100 Fe:100 BaO to ensure satisfactory operation. It should be noted that at temperatures in excess of about 250°—260° C. all of the catalysts, particularly after operational periods of several months duration, are prone to a more or less high extent to a disintegration of the particles which frequently resulted in obstructions of the synthesis tubes. Also with a ratio of 100 Fe:50 BaO at least about 2 parts of copper per 100 parts of iron must be present. Satisfactory operation was only obtained in the 100 Fe: 25 BaO series of experiments.

The results shown in Figure 3 were obtained with a space velocity of 300 v/v/hr. Figure 3 reveals that all of the catalysts of the 100 Fe: 100 BaO series and, therefore, also the copper-rich catalysts, failed within the temperature range provided, that is to say, they required temperatures of about 250° C. for a $CO+H_2$ conversion of about 62% and showed within this range of partial disintegration of the particles resulting in a more or less high pressure drop after a relatively short period of operation. From the 100 Fe:50 BaO series, the only catalyst which showed satisfactory performance was that with 50 Cu. From the 100 Fe:25 BaO series all of the catalysts which contained less than 20 parts of copper per 100 parts of iron failed.

Figure 4 reveals that with the 100 Fe:25 BaO:50 Cu type catalyst even a fourfold and fivefold gas load could be reached within the temperature range provided. The point marked by a cross relates to the fourfold gas load (400 v/v/hr.) whilst that marked by a circle relates to the fivefold gas load (500 v/v/hr.).

Comparative tests were carried out with catalysts in which the same ratio of iron:copper was used, but which contained no supporting material. These catalysts, while giving good results with normal and slightly increased load, likewise showed a gradual disintegration with a threefold to fivefold gas load.

The following Table 3 which is only an extract from the results obtained in a great number of experments, shows that in addition to an increased activity the catalysts in accordance with the invention (10—15 parts BaO and more than 25 parts Cu per 100 parts Fe) have the additional advantage of giving a lower yield of methane in the synthesis product.

TABLE 3.

METHANE FORMATION

	100 Fe 10 Cu	100 Fe 20 Cu	100 Fe 50 Cu
Methane formation with:—			
100 BaO	14.0%	11%	7.5%
50 BaO	11.8%	—	7.0%
25 BaO	10.5%	—	5.5%

(All experiments were carried out at 30 atmospheres with a normal water gas load of 100 v/v/hr.).

Furthermore, it was observed that as the copper content of the catalyst increases an appreciable increase in the yield of oxygen-containing organic compounds takes place, as can also be seen from Table 1. A still further increase in the proportion of oxygen-containing organic compounds was obtained in the case where 50 parts Cu per 100 parts Fe were added.

Moreover, physical measurements revealed that an inner surface area of the reduced catalyst of approximately 10—110 square metres for each gram of present iron is of advantage. The optimum range seems to be that of between about 30 and 80 square metres.

What we claim is:

1. A process for the hydrogenation of carbon monoxide, which comprises passing a synthesis gas containing $CO:H_2$ in the ratio of from 1:0.5 to 1:10 at a temperature in the range 150—300° C. and at a pressure of not less than 10 atmospheres over a reduced catalyst which contains iron, copper, barium and an alkali metal compound, the iron, copper and barium having been co-precipitated from a common solution of salts of the three metals, the barium oxide content of the catalyst being from 10—50 parts, the copper content being more than 25 parts and the alkali-metal content (calculated as K_2O) being more than 2 parts per 100 parts of iron, and more than 50% of the iron in the catalyst being in the metallic state.

2. A process according to Claim 1, in which the temperature is within the range 180°—250° C.

3. A process according to Claim 1 or Claim 2, in which the pressure lies within the range 30—50 atmospheres.

4. A process according to any one of the preceding claims, in which the catalyst contains no supporting material.

5. A process according to any one of Claims 1 to 3, in which the catalyst contains a support constituting not more than 10% by weight of the iron in the catalyst.

6. A process according to any one of the preceding claims, in which the barium and oxide content is within the range 10—30 parts per 100 parts of iron.

7. A process according to any one of the preceding claims, in which the copper content is within the range 50—200 parts, and the alkali-metal content is greater than 5 parts, per 100 parts of iron.

8. A process according to any one of the preceding claims, in which the gas throughput is from 200—500 volumes of gas per volume of catalyst per hour.

9. A process according to any one of the preceding claims, in which more than 75% of the iron is in the metallic state.

10. A process according to any one of the preceding claims, in which the $CO:H_2$ ratio in the synthesis gas is within the range 1:0.5 to 1:1 to give an increase in the yield of oxygen-containing compounds, particularly esters, of high molecular weight.

11. A process according to any one of Claims 1 to 9, in which the $CO:H_2$ ratio in the synthesis gas has a value of less than $\frac{1}{2}$ to give an increase in the yield of alcohols.

12. A process for the production of oxygen-containing organic compounds by the hydrogenation of carbon monoxide in the presence of an iron-copper catalyst activated with barium compound and an alkali-metal compound, substantially as hereinbefore described.

13. An iron catalyst containing copper, barium and an alkali-metal compound with no support or with a support material which constitutes not more than 10% by weight of the iron, the barium oxide content of the catalyst being from 10%—50%, the copper content being more than 25% and the alkali-metal content (calculated as K_2O) being more than 2% based on the total iron content of the catalyst.

14. Oxygen-containing organic compounds and hydrocarbons when produced by the process claimed in any one of Claims 1 to 12.

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Agents for the Applicants.

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SHEETS 1 & 2

Fig. 1

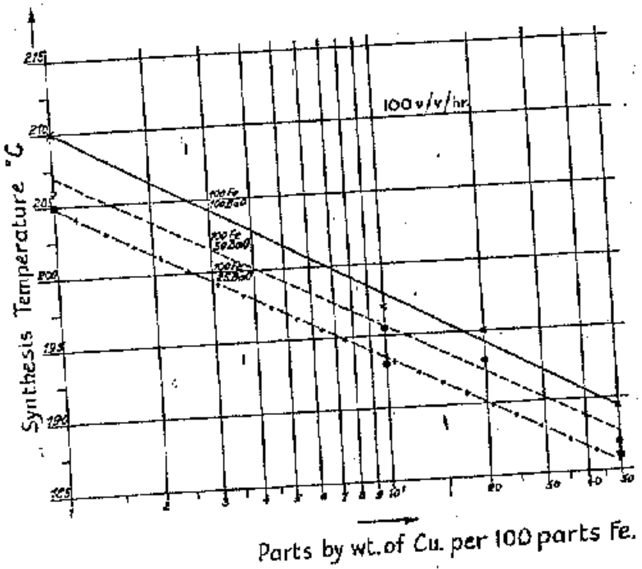


Fig. 2

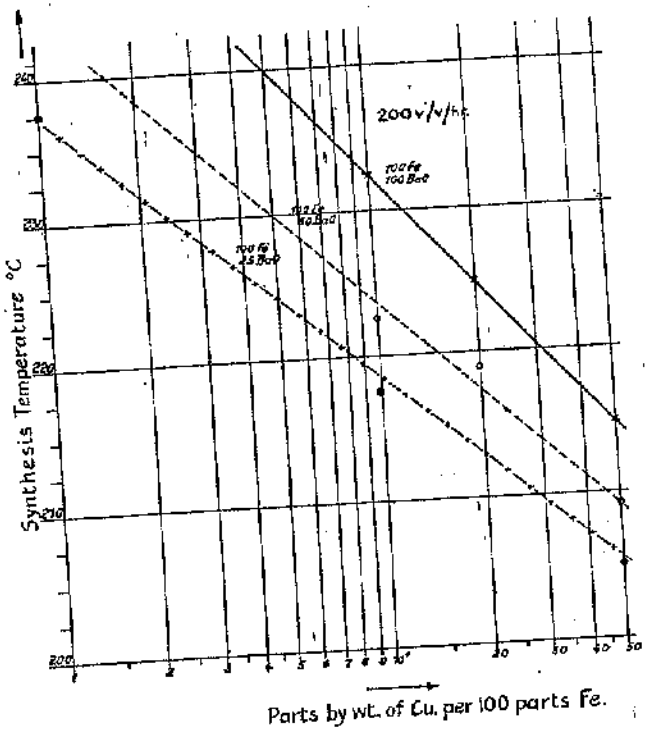
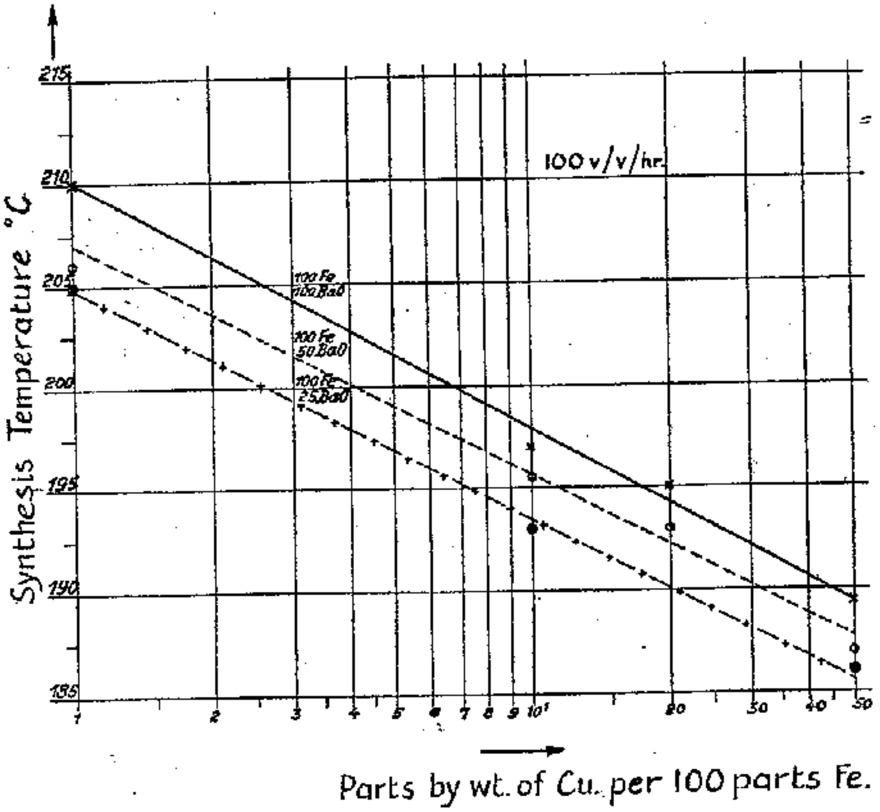


Fig. 1



Synthesis Temperature °C

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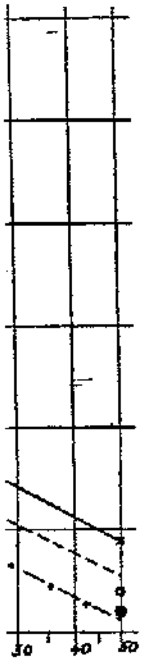
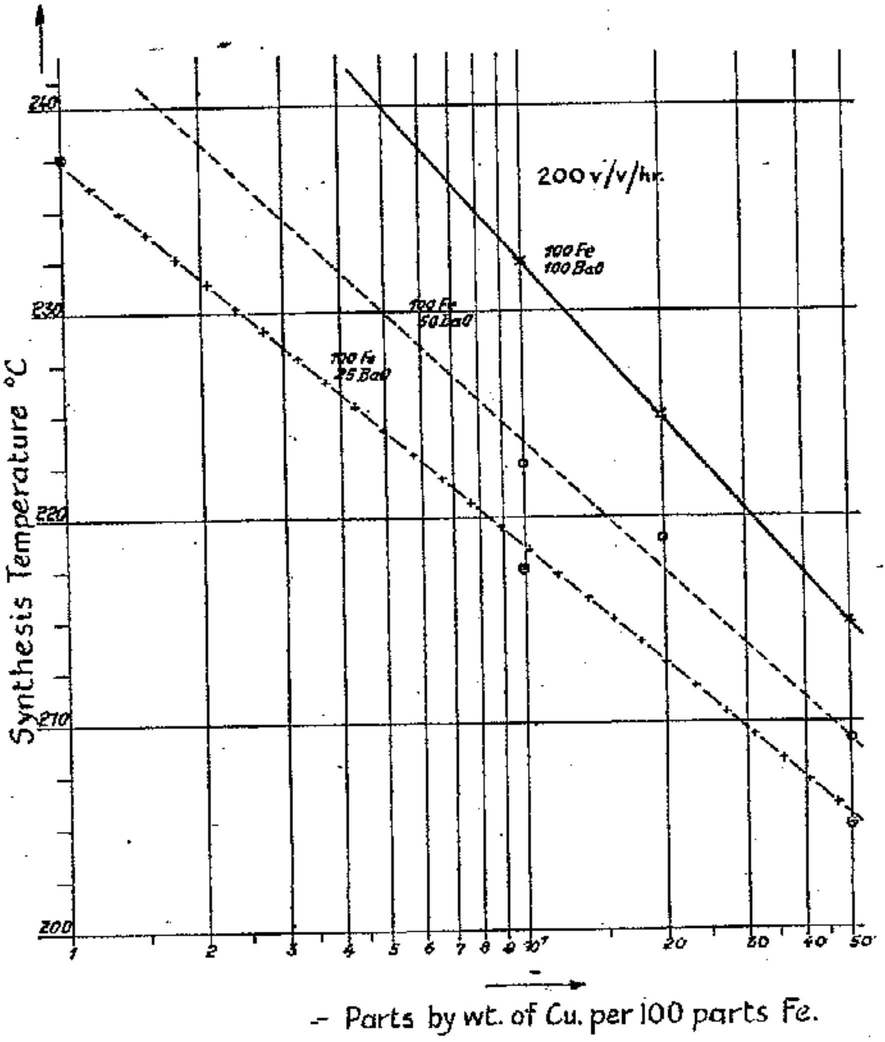
SHEETS 1 & 2



›arts Fe.

Fig. 2



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SHEETS 3 & 4

Fig. 3

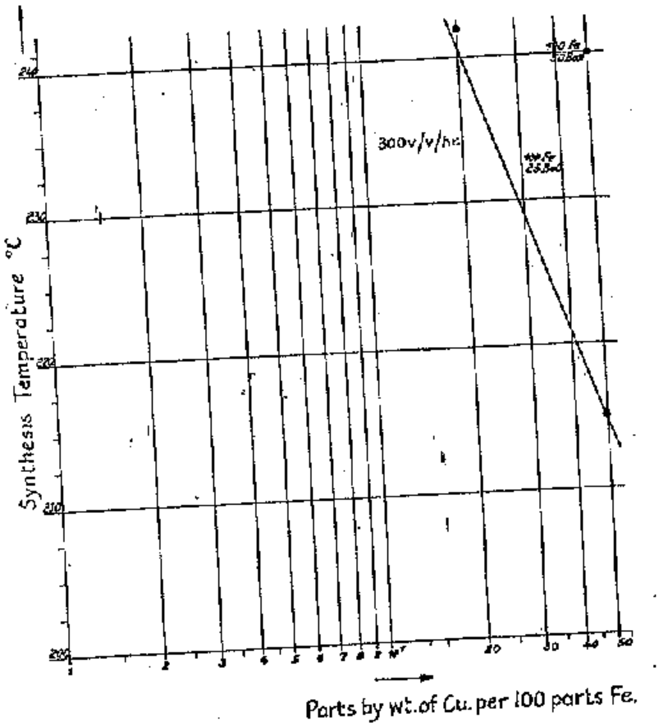


Fig. 4

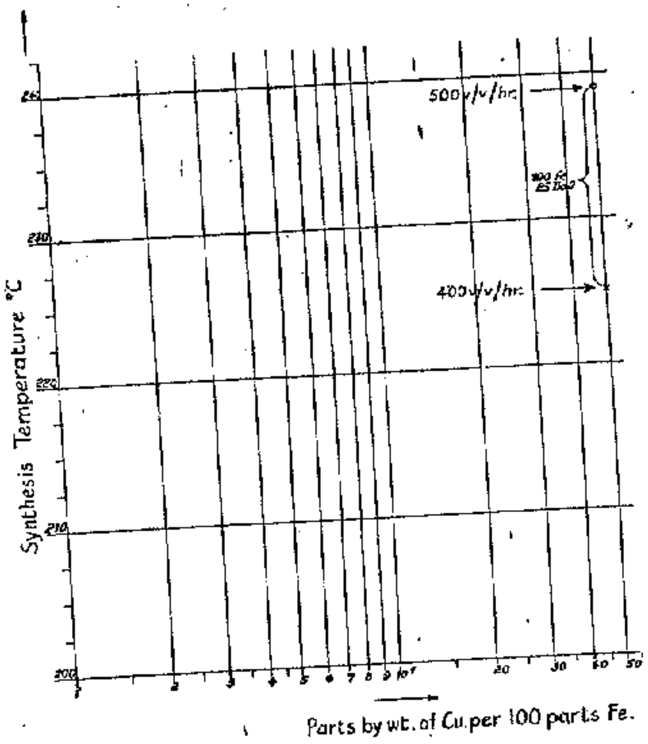
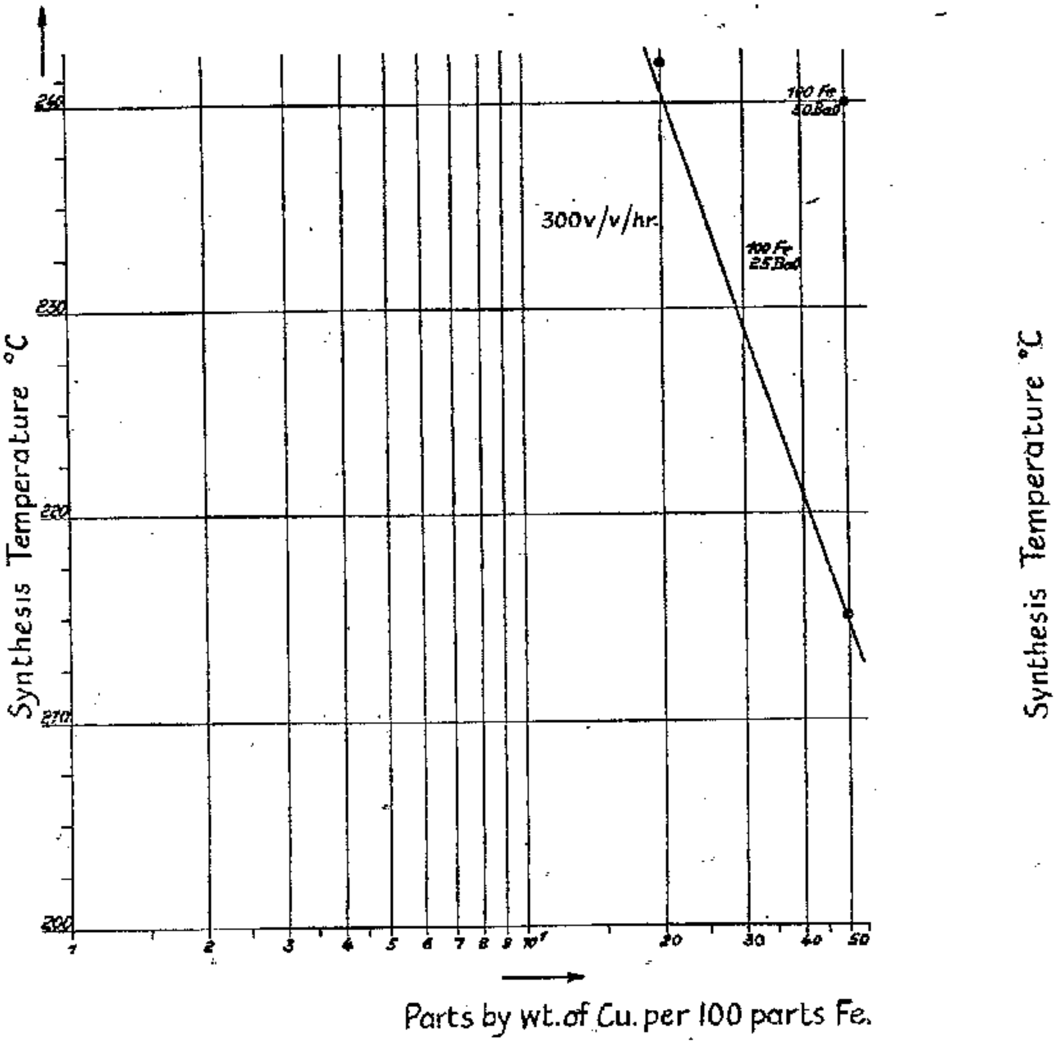


Fig. 3



Synthesis Temperature °C
240
230
220
210
200
300v/v/hr.
100 Fe
50 BaO
100 Fe
25 BaO
1
2
3
4
5
6
7
8
9
10¹
20
30
40
50
Parts by wt. of Cu. per 100 parts Fe.
Synthesis Temperature °C

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SHEETS 3 & 4

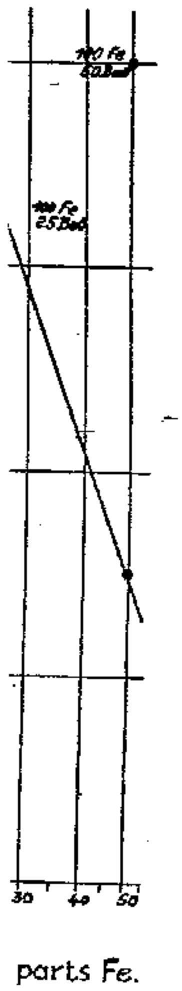

Fig. 4