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FIXATION OF ATMOSPHERIC NITROGEN BY MEANS OF AN ELECTRIC ARC

Emile Briner, Geneva, and Charles Henri Wakker, Conches, Geneva, Switzerland

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Recent researches have established the important part played by electronic action in the production of chemical effects by electric discharges (see E. Briner and A. Rivier, Helv. Chim. Acta, vol. 12, page 881, 1929, in which will be found bibliography relating to the subject). It has indeed been shown that electrons take part in reactions by causing activation of molecules or atoms in the systems traversed by the electric discharge. This is the case, for example, in the formation of oxides of nitrogen by the action of the electric arc on mixtures of nitrogen and oxygen.

This being the case the chemical effects produced by means of an electric discharge should be improved by using as the material of the electrodes a substance which easily yields electrons. In particular these substances may be those which, like the alkaline earth oxides, have a high thermionic emissive power, that is to say, which easily give off electrons at a raised temperature. According to the relationship established by Spanner (Annalen der Physik, vol. 75, page 609, 1924) between the thermionic emissive power and the electronic structure, these substances should preferably be compounds of metals belonging to the groups of the alkali and alkaline earth metals. It has indeed been recognized (compare E. Briner, Boner and Rothen, Helv. Chim. Acta, vol. 9, page 634, 1926 and Journ. Chim. Phys., vol. 23, page 788, 1926) that the formation of oxides of nitrogen from a mixture of nitrogen and oxygen by the action of heat is improved by the presence of a compound such as barium oxide.

It has been proposed by Briner and Rivier to use substances of this kind as coatings on electrodes for use in making oxides of nitrogen by means of an electric arc. (Swiss Specification No. 141,011 and Helv. Chim. Acta, vol. 12, page 88, 1929.) These authors have shown that, in agreement with theoretical predictions, the application to the electrodes of compounds having a high capacity for emitting electrons, such as compounds (oxides or silicates) of alkali metals or alkaline earth metals, improves the yield of oxides of nitrogen in the fixation of nitrogen as oxide by means of the electric arc. The process, however, is open to the objection that the coatings of the active compounds do not adhere sufficiently to the electrodes during the long periods of operation of the arc required in an industrial process.

By the present invention the fixation of nitrogen by means of the electric arc is improved if there are used for the production of the arc electrodes consisting of an alloy of metals of a specific weight of at least 5 with metals from the first and second group of the periodic system and of a specific weight below 4. Metals of a specific weight of at least 5 are for instance copper, nickel, iron, etc. Metals of a specific weight below 4 are alkali metals, (such as sodium, lithium, etc.) or alkaline earth metals (such as calcium, strontium, etc.). This latter group has in fact a very high power of emitting electrons and a very low ionization potential. For this reason they yield very easily electrons whose action determines to a greater or less extent the chemical reactions produced by means of the electric discharge. It has in fact been found that the use of electrodes in accordance with the invention leads to very appreciable improvements in the yield in the fixation of nitrogen in the form of oxides by the action of the arc on a mixture of nitrogen and oxygen. Illustrations of these improvements follow hereinafter.

It may here be noted that advantage has already been taken of the ease with which electrons are emitted by alkali and alkaline earth metals in the manufacture of cathodes for wireless transmitting apparatus, for luminescent tubes in illuminated signs and for sparking plugs for internal combustion engines. Concerning the application of the electrical discharge to chemical action, which application comes into question in the present invention, reference may be made to U. S. Patent 1,266,717, relating to a process for producing oxides of nitrogen by means of the electric arc. The essential feature of the process of that specification is the use of aluminium or silicon as the metal for the electrode; it is stated that the electrodes may also contain alkali or alkaline earth metals, these metals giving rise to the formation of oxides which promote the formation of oxides of nitrogen.

The improvement attained by the present invention, on the contrary, is due essentially to the use of alkali or alkaline earth metals, the part played by which in chemical reactions produced by the electric discharge is easily explicable on the basis of the considerations hereinbefore referred to.

In carrying out the invention the alkali or alkaline earth metal may be alloyed with any metal of a specific weight of at least 5, such as copper, nickel or iron, which are customarily used as electrodes in electric arc furnaces for fixing nitrogen in the form of oxides; in U. S.

Patent No. 1,517,727 silver is mentioned as useful.

Further also alloys of these heavy metals, such as chromium-nickel steels, nickel-copper alloys (Monel metal) etc., alloyed with alkali and alkaline earth metals, may be used. On the other hand more than one alkali or alkaline earth metal may be present in an electrode. It is also not absolutely necessary that in an electric arc both electrodes must consist of the alloy disclosed in this invention, since one such electrode in combination with one of the hitherto usual electrodes, will already yield a good effect.

Excluded from the metals from which the electrodes are to be produced for the purpose of the invention are aluminium and silicon and alloys thereof, since the yields which have been obtained with electrodes made from these metals are somewhat low.

The favorable action of the alkali and alkaline earth metals in the process of the invention may be seen from the following results, but we do not limit ourselves to the metal combinations mentioned by way of examples, and it is to be understood that other combinations come within the scope of the invention:—

The action of an arc of 140 milliamperes on air at atmospheric pressure

Electrode	Output in liters per hour	Potential of the arc in volts	Percentage improvement in the utilization of energy in the fixation of nitrogen
	Liters		*Percent*
Cu	25	957	
Cu-Li (0.8% Li)	25	805	58
Cu-Li (1.7% Li)	25	590	97
Cu-Li (3% Li)	25	495	158
Cu-Ca (1.5% Ca)	40	700	69
Cu-Ca-Li (1% Ca and 1% Li). Example of a ternary alloy	25	480	116
Cu-Ba (0.9% Ba)	25	935	46
Ag	40	687	
Ag-Li (4% Li)	40	610	51

Similar improvements have also been observed in a more powerful apparatus operating with a current of 3 amperes and a power of 2–3 kilowatts instead of 140 milliamperes and 80–140 watts as in the preceding table.

The results were as follows:—

Electrode	Output in liters per hour	Potential of the arc in volts	Percentage improvement in the utilization of energy in the fixation of nitrogen
			Percent
Cu	5.7	1,070	
Cu-Li (1.7% Li)	5.7	750	78
Cu-Li (3% Li)	5.7	650	108

It will be seen from the foregoing tables that the improvements attained are very substantial and may amount to nearly 160 per cent.

It must be noted that the improvements cannot be attributed to a variation in the power factor of the arc for, as is known, this factor is scarcely affected by substituting the alloy for the pure metal.

The diminution in the potential attained by the use of the electrodes used in accordance with the invention has the effect of decreasing the output of energy; consequently the temperature of the gases is lower and the decomposition of the oxides of nitrogen is less, so that there is an improvement in the yield with respect to the consumption of electrical units.

The presence of an alkali or alkaline earth metal in the electrodes substantially increases the stability of the arc.

Finally it has been established that, far from promoting wear of the electrodes, the presence in the electrodes of alkali or alkaline earth metals in the small proportions found to be favorable imparts to them an increased resistance to wear. For example when a mixture of nitrogen and oxygen is subjected to the action of an arc between electrodes of copper, the electrodes are oxidized to a less extent when they contain calcium than when they consist of pure copper. It should be noted that the alkali metals and alkaline earth metals whose use is contemplated by the invention are actually available cheaply in commerce.

The addition of alkali and alkaline earth metals, to the electrodes in accordance with the invention thus manifests itself in

(1) an improvement in the utilization of energy in the fixation of the nitrogen as oxides of nitrogen;

(2) an increase in the concentration of the nitrogenous products and

(3) a much greater stability of the arc.

The invention thus leads to a marked improvement over the hitherto known processes for the fixation of nitrogen by means of the electric arc.

What we claim is:—

1. A process for the fixation of atmospheric nitrogen by means of an electric arc, wherein the arc is produced by means of electrodes consisting of an alloy of at least one of the metals selected from the group comprising copper, nickel, iron, silver, with metals selected from the group comprising sodium, lithium, calcium, strontium, barium.

2. A process for the production of oxides of nitrogen from a mixture of nitrogen and oxygen by means of an electric arc, wherein the arc is produced by means of electrodes consisting of an alloy of at least one of the metals selected from the group comprising copper, nickel, iron, silver, with metals selected from the group comprising sodium, lithium, calcium, strontium, barium.

EMILE BRINER.
CHARLES HENRI WAKKER.