[Second Edition.]

PATENT SPECIFICATION

345,649

Application Date: Sept. 18, 1929. No. 28,268/29.

Complete Left: July 18, 1930.

Complete Accepted: March 18, 1931.

72

PROVISIONAL SPECIFICATION.

Improvements in or relating to Catalytic Processes.

We, BRITISH CELANESE LIMITED, a Company incorporated in accordance with the laws of Great Britain, of Celanese House, 22 & 23, Hanover Square, London, W. 1, WALTER BADER, a citizen of the Swiss Republic, and EDWARD BOADEN THOMAS, a subject of the King of Great Britain, both of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention to be as follows:—

This invention is concerned with the catalysing of chemical reactions, more particularly by means of contact masses comprising oxides and hydroxides of metals or mixtures of such oxides or hydroxides.

Oxides of metals are, as is well known, commonly employed as catalysts in carrying out many chemical reactions, for example reactions involving oxidation, reduction, hydrogenation, dehydration and so on. Such oxides can be and have been prepared by very widely varied methods, but it is well known that the catalytic activity of a given oxide or mixture of oxides can vary within very wide limits depending upon the method of preparation, and especially upon whether or not impurities are present even in exceedingly small quantities. Oxides or hydroxides prepared from solutions of the corresponding metal salts by processes involving treatment with precipitants are frequently, so far as their physical condition is concerned, very suitable for the preparation of catalytic masses, but are very difficult to obtain free from traces of alkalies or other precipitating agents. Even though it may be possible to remove such alkali or other agent completely the process involved may be so drastic as to effect in no small degree the physical properties and catalytic activity of the product.

We have found that metal oxides or hydroxides prepared from solutions of suitable metallic salts by introducing hydroxyl ions by an electrolytic process are particularly suitable as catalysts or as constituents of catalysts for catalysing chemical reactions for example the synthesis of methyl alcohol from carbon monoxide and hydrogen. Thus for example, by the passage of an electric current, hydroxyl ions may be caused to pass, by way of a membrane permeable thereto, from a solution containing them into a solution of a metallic salt where they unite with metallic ions to form the desired hydroxides or oxides. The metal oxides and hydroxides may thus be prepared from solutions of metallic salts in the absence of alkali metal ions and the presence of alkali metal compounds in the product avoided.

The production of the metal oxides or hydroxides may, for instance, be conveniently carried out in an apparatus comprising a suitable container for liquid within which are disposed electrodes connected to a source of direct current and which are separated by means of a suitable diaphragm which permits the passage of hydroxyl ions but which is substantially impermeable to the ions of the metal or metals in question. The solution containing the metal salt or salts is introduced into the anode compartment of the cell, while the cathode compartment contains an electrolyte capable of yielding hydroxyl ions, for example an alkali carbonate. Upon passing a uni-directional electric current through the cell, oxides, hydrated oxides, or hydroxides of the metal or metals accumulate on the anode side of the diaphragm. The acid corresponding with the metal salt or salts employed is simultaneously liberated at the anode, and in order to prevent such acid from diffusing towards the cathode a second diaphragm may very advantageously be inserted between the anode and the aforesaid cathode diaphragm. The acid liberated in the anode compartment may then be removed in any convenient manner without interfering with the action of the remaining parts of the electrolytic cell, for example by passing fresh water continuously or intermittently through the said compartment.

The shape of the cell and of the electrodes and diaphragm and the disposition of the same can be adapted to any desired manner of working. For example, electrodes and diaphragms may be vertical

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Oxides of metals are, as is well known, commonly employed as catalysts in carrying out many chemical reactions, for example reactions involving oxidation, reduction, hydrogenation, dehydration and so on. Such oxides can be and have been prepared by very widely varied methods, but it is well known that the catalytic activity of a given oxide or mixture of oxides can vary within very wide limits depending upon the method of preparation, and especially upon whether or not impurities are present even in exceedingly small quantities. Oxides or hydroxides prepared from solutions of the corresponding metal salts by processes involving treatment with precipitants are frequently, so far as their physical condition is concerned, very suitable for the preparation of catalytic masses, but are very difficult to obtain free from traces of alkalies or other precipitating agents. Even though it may be possible to remove such alkali or other agent completely the process involved may be so drastic as to effect in no small degree the physical properties and catalytic activity of the product.

We have found that metal oxides or hydroxides prepared from solutions of suitable metallic salts by introducing hydroxyl ions by an electrolytic process are particularly suitable as catalysts or as constituents of catalysts for catalysing chemical reactions for example the synthesis of methyl alcohol from carbon monoxide and hydrogen. Thus for example, by the passage of an electric current, hydroxyl ions may be caused to pass, by way of a membrane permeable thereto, from a solution containing them into a solution of a metallic salt where they unite with metallic ions to form the desired hydroxides or oxides. The metal oxides and hydroxides may thus be prepared from solutions of metallic salts in the absence of alkali metal ions and the presence of alkali metal compounds in the product avoided.

The production of the metal oxides or hydroxides may, for instance, be conveniently carried out in an apparatus comprising a suitable container for liquid within which are disposed electrodes connected to a source of direct current and which are separated by means of a suitable diaphragm which permits the passage of hydroxyl ions but which is substantially impermeable to the ions of the metal or metals in question. The solution containing the metal salt or salts is introduced into the anode compartment of the cell, while the cathode compartment contains an electrolyte capable of yielding hydroxyl ions, for example an alkali carbonate. Upon passing a uni-directional electric current through the cell, oxides, hydrated oxides, or hydroxides of the metal or metals accumulate on the anode side of the diaphragm. The acid corresponding with the metal salt or salts employed is simultaneously liberated at the anode, and in order to prevent such acid from diffusing towards the cathode a second diaphragm may very advantageously be inserted between the anode and the aforesaid cathode diaphragm. The acid liberated in the anode compartment may then be removed in any convenient manner without interfering with the action of the remaining parts of the electrolytic cell, for example by passing fresh water continuously or intermittently through the said compartment.

The shape of the cell and of the electrodes and diaphragm and the disposition of the same can be adapted to any desired manner of working. For example, electrodes and diaphragms may be vertical

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or they may be horizontal or disposed in any other desired manner.

The electrodes may be of any convenient materials which are capable of resisting the electrolytic or other reactions taking place in the cell, for example the anode may be constructed of magnetite while a cathode of a suitable metal has been found very satisfactory. In order to obtain as pure a product as possible the electrodes should be of such materials as will not lead to the introduction of impurities into the oxides or hydroxides to be prepared.

The diaphragm separating the cathode from the rest of the cell may be constructed of a material inherently capable of preventing substantially the passage of the metallic ions while permitting the passage of hydroxyl ions, for example it may be constructed of suitable porous plate. It has been found that highly satisfactory diaphragms may be prepared from supports of very many porous materials, for example fabrics, porous stoneware, and the like by depositing thereon a suitably finely divided material or material of suitably small pore dimension so as to produce a diaphragm of the desired character.

Such deposition of finely divided material or material of suitably small pore dimension may be effected in any desired manner, for example reagents may be caused to react so as to form a deposit of a suitable material on or in a porous plate, fabric, or the like. Thus for instance two reagents may be allowed to diffuse, one from either side, into a plate of porous stoneware and to interact therein. Deposition of suitable material on or in a support may however be very conveniently effected by making use of the phenomenon of cataphoresis. Thus, for example, a cathode diaphragm of fabric or porous earthenware may be disposed in a cell provided with suitable electrodes, a suspension of the finely divided material being placed on the anode side of the diaphragm. Under the influence of a potential gradient between the anode and the cathode the particles move towards the cathode and accumulate on the diaphragm, the operation being continued until a quantity of material sufficient to block the pores to the desired extent has been deposited. Any desired finely divided material may be employed for the preparation of the diaphragms in this manner, but it should not, of course, be such as would be objectionable in the metal oxides or the like subsequently to be produced. Very conveniently there may be employed a suspension of the same oxide or oxides which are to be produced. This deposition of the finely divided material may be effected in the cell in which the production of oxides or hydroxides is subsequently to take place.

In order to give some indication of the pore size of the cathode diaphragms which may be used in accordance with the invention it may be mentioned that a pore size of the same order as that of the semi-permeable membranes of parchment, copper ferrocyanide, or the like, commonly employed in exhibiting and measuring osmotic pressures is very suitable. The invention is not limited, however, to the employment of diaphragms of this character.

The metal oxides or hydroxides accumulating on the diaphragm when the cell is in action may be removed continuously or intermittently as desired, for example by means of suitable scrapers. For instance, the cathode diaphragm may form the surface of a slowly rotating cylinder from which a scraper continuously removes the coating of hydroxides or oxides. Where the diaphragm has been prepared by the deposition of finely divided material upon a material of substantially larger pore size, it has been found very advantageous to protect the diaphragm by a protective screen of comparatively wide mesh disposed close to the diaphragm and on the anode side thereof. When the accumulation of oxides or hydroxides has become sufficient to cover both diaphragm and protective screen it may readily be removed from the surface of the latter by suitable means without destroying the coating on the diaphragm.

The chemical and physical character of the oxides or hydroxides may be varied, according to the precise reaction they are required to catalyse by suitably adjusting the conditions of precipitation, more particularly as regards the concentration and temperature of the solution, the current density and the presence or absence of carbon dioxide.

In this manner there may be prepared any desired insoluble or difficultly soluble oxides or hydroxides of metals or mixtures of such oxides or hydroxides. They may be obtained remarkably free from impurities, particularly alkali metals. They are also obtainable in highly colloidal form which particularly suits them for the preparation of catalysts for use in effecting chemical reactions. For catalysing chemical reactions in accordance with the invention they may be subjected to any desired drying, calcining, reducing and like processes or may be admixed with other substances, e.g. metal powders or acidic oxides, or they may be placed on suitable carriers or supports. Thus catalysts particularly suitable for the preparation of methanol from hydrogen and carbon monoxide may, for example, be prepared from a zinc hydroxide or a mixture of zinc hydroxide with chromium hydroxide prepared in the manner described.

The following example illustrates the preparation of metal oxides and hydroxides and the preparation therefrom of the catalytic agents used in accordance with the invention.

EXAMPLE.

A cell of glass or ebonite is divided into three compartments by two diaphragms of closely woven linen fabric, the middle compartment being of larger capacity than the two outer ones. In one of the outer compartments the anode, consisting of a magnetite plate, is suspended. A slow stream of water is admitted at the bottom of this compartment, and an overflow is provided. The other outer compartment contains a sheet of zinc which serves as the cathode. In the middle compartment a screen of wide-mesh fabric is adjusted at a short distance from the cathodic diaphragm, so as to protect the coating of metal hydroxide nearest to the diaphragm from any mechanical disturbance.

The whole cell is filled with water. Some sodium carbonate, e.g. 0.1% is added to the cathodic liquid, and a suspension of colloidal zinc hydroxide and chromic hydroxide to the middle compartment, where it is kept in suspension by bubbling air through or by an agitator. Direct current of 120 volts is applied to the cell, which causes the suspended particles to adhere to the cathodic diaphragm. When a coat of sufficient density has been formed, a solution of zinc nitrate and chromium nitrate, containing 3 to 4 atoms of zinc for 1 atom of chromium, is admitted into the middle compartment at such a rate that a current density at the cathode of about 2 amps. per square dm. is maintained. The temperature of the solution may be controlled so that it is maintained at or slightly above that of the atmosphere. The cathodic diaphragm becomes covered with a coat of slimy, purplish-grey or greenish precipitate, which eventually grows through the protecting screen and may be periodically removed therefrom by scrapers, without interrupting the work of the cell, which thus continuously produces the mixed hydroxides.

The precipitate removed from the cell may be washed, thickened by filtering or pressing, shaped into pellets or beads, dried, heated in a reducing atmosphere, and is then ready for use as a catalyst in the synthesis of methanol.

Dated this 17th day of September, 1929.
WHITEHEAD & STEPHENS,
Chartered Patent Agents,
Celanese House, 22 & 23, Hanover Square,
London, W. 1.

COMPLETE SPECIFICATION.

Improvements in or relating to Catalytic Processes.

We, BRITISH CELANESE LIMITED, a Company incorporated in accordance with the laws of Great Britain, of Celanese House, 22 & 23, Hanover Square, London, W. 1, WALTER BADER, a citizen of the Swiss Republic, and EDWARD BOADEN THOMAS, a subject of the King of Great Britain, both of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is concerned with the catalysing of chemical reactions, more particularly by means of contact masses comprising oxides and hydroxides of metals or mixtures of such oxides or hydroxides.

Oxides of metals are, as is well known, commonly employed as catalysts in carrying out many chemical reactions, for example reactions involving oxidation, reduction, hydrogenation, dehydration and so on. Such oxides can be and have been prepared by very widely varied methods, but it is well known that the catalytic activity of a given oxide or mixture of oxides can vary within very wide limits depending upon the method of preparation, and especially upon whether or not impurities are present even in exceedingly small quantities. Oxides or hydroxides prepared from solutions of the corresponding metal salts by processes involving treatment with precipitants are frequently, so far as their physical condition is concerned, very suitable for the preparation of catalytic masses, but are very difficult to obtain free from traces of alkalies or other precipitating agents.

the presence of which may have a profound effect upon the behaviour of the product as a catalyst. Even though it may be possible to remove such alkali or other agent completely the process involved may be so drastic as to affect in no small degree the physical properties and catalytic activity of the product.

We have found that the metal oxides or hydroxides prepared from solutions of suitable metallic salts by interaction of metal ions and hydroxyl ions in an electrolytic process, are particularly suitable as catalysts or as constituents of catalysts for catalysing chemical reactions, for example the synthesis of methyl alcohol from carbon monoxide and hydrogen.

In preparing the metal oxides or hydroxides the actual source of the hydroxyl ions is immaterial. It may be external to the solution of a metal salt being subjected to electrolysis or the metal salt solution itself may supply the hydroxyl ions. Thus for example by the passage of an electric current, hydroxyl ions may be caused to pass, by way of a membrane permeable thereto, from a solution containing them into the solution of a metallic salt. In any case the hydroxyl ions unite with metallic ions to form the desired hydroxides or oxides.

As the metal oxides or hydroxides may thus be prepared from solutions of metallic salts without the aid of precipitants, such as alkali metal compounds, they may be obtained substantially free from alkali metals or other impurities. Catalytic agents consisting of or containing the said electrolytically prepared metal oxides or hydroxides are thus of great value in that they enable reactions to be carried out in the presence of metal oxides or hydroxides, but in absence of alkali metal compounds. A further advantage is that catalytic agents may be prepared containing small but accurately known proportions of alkali metal compound by the simple expedient of adding the requisite proportion.

The metal oxides or hydroxides prepared in the manner described may be used, either alone or in admixture with other substances, for catalysing a wide range of chemical reactions, for example reactions involving oxidation, reduction, hydrogenation or dehydration. In particular zinc oxide or a mixture of zinc and chromium oxides prepared in the aforesaid manner has been found especially valuable as catalyst in the manufacture of methyl alcohol from carbon monoxide and hydrogen, in that the simultaneous formation of products containing more carbon atoms than methyl alcohol does not take place to any material extent. The catalyst may contain zinc and chromium in the proportion of about three to four atoms of the former to one atom of the latter.

The production of the metal oxides or hydroxides may, for instance, be carried out in an apparatus comprising a suitable container for liquid within which are disposed electrodes connected to a source of direct current and which are separated by means of a suitable diaphragm which permits the passage of hydroxyl ions but which is substantially impermeable to the ions of the metal or metals in question. The solution containing the metal salt or salts is introduced into the anode compartment of the cell, while the cathode compartment contains an electrolyte capable of yielding hydroxyl ions, for example an alkali carbonate. Upon passing a uni-directional electric current through the cell under sufficient potential, oxides, hydrated oxides, or hydroxides of the metal or metals accumulate on the anode side of the diaphragm. The acid corresponding with the metal salt or salts employed is simultaneously liberated at the anode, and in order to prevent such acid from diffusing towards the cathode a second diaphragm may very advantageously be inserted between the anode and the aforesaid cathode diaphragm. The acid liberated in the anode compartment may then be removed in any convenient manner without interfering with the action of the remaining parts of the electrolytic cell, for example by passing fresh water continuously or intermittently through the said compartment.

The shape of the cell and of the electrodes and diaphragm and the disposition of the same can be adapted to any desired manner of working. For example, electrodes and diaphragms may be vertical or they may be horizontal or disposed in any other desired manner.

The electrodes may be of any convenient materials which are capable of resisting the electrolytic or other reactions taking place in the cell, for example the anode may be constructed of magnetite while a cathode of metal has been found very satisfactory. In order to obtain as pure a product as possible the electrodes should be of such materials as will not lead to the introduction of impurities into the oxides or hydroxides to be prepared.

The diaphragms impervious to metallic ions used to separate the cathode from the rest of the cell, may be constructed of a material inherently capable of preventing substantially the passage of the metallic ions while permitting the passage of hydroxyl ions, for example they may be constructed of suitable porous plate. It has however, been found that such diaphragms may comprise supports of porous materials, for example fabrics or porous stoneware, having deposited thereon a suitable finely divided material or material of suitably small pore dimension.

The deposition of finely divided material or material of suitably small pore dimension on supports may be effected for instance by chemical means or by making use of the phenomenon of cataphoresis. Thus, for example, a cathode diaphragm of fabric may be immersed in a suspension of the material between electrodes, the suspended material depositing on the support under the influence of the potential gradient between the electrodes. Any desired finely divided material may be employed for the preparation of the diaphragms in this manner, but it should not, of course, be such as would be objectionable in the metal oxides or the like subsequently to be produced. Very conveniently there may be employed a suspension of the same oxide or oxides which are to be produced.

The metal oxides or hydroxides accumulating on the diaphragm when the cell is in action may be removed continuously or intermittently as desired, for example by means of suitable scrapers. Where the diaphragm has been prepared by the deposition of finely divided material upon a material of substantially larger pore size, it may be protected by a screen of comparatively wide mesh disposed close to the anode side thereof. When the accumulation of oxides or hydroxides has become sufficient to cover both diaphragm and protective screen it may readily be removed from the surface of the latter by suitable means without destroying the coating on the diaphragm.

The special provision of a diaphragm impermeable to metallic ions and the presence, adjoining the cathode of a solution containing hydroxyl ions are not however essential in the production of the metal oxides or hydroxides from solutions of metal salts.

If for example the said diaphragm and solution containing hydroxyl ions are omitted it is found that the production of oxides or hydroxides may nevertheless still be effected, with advantages consequent upon the simplification of the apparatus. It appears possible that in the simplified apparatus a layer or film of oxides or hydroxides forms on the cathode and that the formation of hydroxides or oxides in the cell then proceeds. A diaphragm surrounding the anode is advisable, as before, to prevent the acid liberated at the anode from diffusing into the cell and re-dissolving the oxides or hydroxides.

According to the simplified process therefore, the metal oxides or hydroxides may be produced simply by the passage of a unidirectional electric current through solutions of metal salts. As in the case where a diaphragm impervious to the metallic ions is utilised, the current may be passed between electrodes resistant to the solution employed and to the electrolytic processes occurring within the cell. Electrodes of the character previously mentioned have been found highly satisfactory, for example anodes of magnetite and cathodes of metal. The acid liberated at the anode is conveniently removed by surrounding the anode with a porous diaphragm, for example of filter cloth, and intermittently or continuously drawing off from the anode compartment so formed the acid appearing therein. The oxides or hydroxides formed or liberated in the cell may be removed continuously or intermittently in any desired manner. A very convenient method is by circulating the metal salt solution undergoing electrolysis between the electrolytic cell and a settling tank in which the hydroxides or oxides may be allowed to settle out. The concentration of the metal salt or salts in the circulating salt solution may be maintained at the desired or requisite value by periodic or continuous addition of metal salt solution of suitable concentration to the circulating liquid.

Where cooling of the cell is necessary this may conveniently be accomplished by circulating the cell liquid through a cooling coil or other device cooled for example by means of ice or cold brine. Very efficient cooling may be secured in this manner with the advantage that high current densities may be employed in the cell without excessive rise of temperature.

The above method of separating the metal oxides or hydroxides from the electrolysed liquid, and/or the above method of cooling may of course equally well be utilised when the electrolysed cell is provided with a diaphragm impervious to metallic ions.

In conducting the production of the metal oxides or hydroxides utilised in accordance with the invention the electromotive force employed and the current density may vary within wide limits. The electromotive force should always be in excess of that which deposits only metal from the salt solution employed. In practice it is found that an EMF of about 30 volts yields very satisfactory results when zinc hydroxide chromium hydroxide and other heavy metal hydroxides are to be produced, an EMF of 20 volts being about the practicable minimum. Higher voltages may be employed if desired though generally with reduced electrical efficiency. The maximum current density permissible is largely dependent upon the efficiency of the cell cooling devices as in general it is best to liberate or form the metal oxides or hydroxides at a comparatively low temperature.

In operating the process therefore, it is convenient to use a source of current of the desired voltage, say 30 volts, and then to adjust the concentration of the salt solution undergoing electrolysis until the current which flows is as high as is compatible with the maintenance of the temperature at the required low value.

Particularly valuable highly colloidal products may be produced by effecting the electrolytic treatment of metal salts at low temperatures, e.g. temperatures below 30° C.

Any desired insoluble or difficultly soluble oxides or hydroxides of metals, or mixtures or even compounds of two or more such oxides or hydroxides may be produced by treating electrolytically solutions of appropriate soluble metal salts or mixtures of metal salts, for example salts of zinc, chromium, or cobalt. As regards the metal salts employed the nitrates have been found especially useful as any nitrate appearing in the separated oxides or hydroxides is fairly readily eliminated when the products are heated. Other soluble salts may however be employed, for example formates. If desired the metal oxides or hydroxides obtained may be subjected, prior to use as catalysts, to further treatment for elimination of any nitrate or other anion derived from the salt employed. Such elimination may for instance be effected by electrolysis.

As previously indicated the metal oxides or hydroxides may be obtained in the manner described, particularly free from alkali metals. They are also obtainable in highly colloidal form which particularly suits them for the preparation of catalysts. For catalysing chemical reactions in accordance with the invention they may be subjected to any desired treatment in order to bring them into a suitable form. For example they may be placed upon carriers or supports and/or dried, calcined, or reduced, or mixed with other substances, e.g. metal powders or acidic oxides, or otherwise treated according to the well known methods of preparing catalytic agents from other forms of metal oxides and hydroxides. The catalytic agents may be employed for catalysing chemical reactions in the same manner as catalytic agents consisting of or containing oxides or hydroxides prepared by methods other than electrolysis of solutions of the corresponding metal salts.

The following examples illustrate the preparation of metal oxides and hydroxides and the preparation therefrom of catalytic agents used in accordance with the invention.

Example 1.

A cell of glass or ebonite is provided with a magnetite anode surrounded by a diaphragm of filter cloth in the form of a flat bag. Means are provided for withdrawing liquid from the anode compartment so formed. The cell is also provided with a zinc cathode, and the cathode compartment is provided with an overflow near the top and an inlet near the bottom, the latter conveniently in the form of a tube dipping into the cell contents and extending nearly to the bottom of the cell.

The electrodes are connected to a source of direct current of about 30 volts E.M.F. and a dilute solution of zinc and chromium nitrates, containing 3 to 4 atoms of zinc to one atom of chromium, is allowed to flow through the cell from the inlet to the overflow. The escaping liquid contains highly colloidal zinc and chromium oxides in suspension and is led into a settling tank in which the hydroxides settle out. The supernatant liquid is led through a coil kept cool by ice and is then returned to the cell which is thus maintained at about 15 to 20° C.

From the anode compartment dilute nitric acid is continuously withdrawn. To the overflow from the cathode compartment there is added continuously a solution of zinc and chromium nitrates sufficient to make good the water withdrawn as dilute nitric acid from the anode compartment, the small quantities of metal salts carried away in the dilute nitric acid, and the metal salt used up in the formation of the metal hydroxides.

The concentration of the salt solution passing through the cell is maintained at such a value that the resistance of the cell and the current corresponding thereto do not give rise to greater development of heat than that with which the cooling devices are capable of coping. With electrodes about 2 centimetres apart and an E.M.F. of 30 volts the current density may be about 2 amperes per square decimetre.

If desired a number of cells may be operated simultaneously, preferably in parallel connection. The overflows, consisting of electrolysed metal salt solution with metal oxide or hydroxide in suspension, may be passed to a single settling tank, and the supernantant liquid then passed through a cooling device and redistributed to the various cells, if necessary after adjustment of metal salt content.

For operating in parallel a bank of cells may very advantageously be made up from a number of plates of insulating material spaced apart by U shaped members of similar material, the whole being clamped together after the manner of the plates of a filter press. Each U shaped member may be provided with overflow spout or pipe near the upper end of one arm, and a tube may pass through the lower part for attachment, on the inside of the U member to a filter cloth bag surrounding the anode. By means of this tube the acid appearing at the anode may be withdrawn as required. Each cell may be provided with a tube, dipping almost to the bottom, for the admission of the salt solution. In the cells the electrodes may be supported by means of lugs formed thereon and adapted to rest on the upper ends of the U shaped distance pieces forming the bottom and end wall of each cell.

Example 2.

A cell of glass or ebonite is divided into three compartments by two diaphragms of closely woven linen fabric, the middle compartment being of larger capacity than the two outer ones. In one of the outer compartments the anode, consisting of a magnetite plate, is suspended. A slow stream of water is admitted at the bottom of this compartment, and an overflow is provided. The other outer compartment contains a sheet of zinc which serves as the cathode. In the middle compartment a screen of widemesh fabric is adjusted at a short distance from the cathodic diaphragm, so as to protect the coating of metal hydroxide nearest to the diaphragm from any mechanical disturbance.

The whole cell is filled with water. Some sodium carbonate, e.g. 0.1% is added to the cathodic liquid, and a suspension of colloidal zinc hydroxide and chromic hydroxide to the middle compartment, where it is kept in suspension by bubbling air through or by an agitator. Direct current of 120 volts is applied to the cell, which causes the suspended particles to adhere to the cathodic diaphragm. When a coat of sufficient density has been formed, a solution of zinc nitrate and chromium nitrate, containing 3 to 4 atoms of zinc for 1 atom of chromium, is admitted into the middle compartment at such a rate that a current density at the cathode of about 2 amps. per square dm. is maintained. The temperature of the solution may be controlled so that it is maintained at or slightly above that of the atmosphere. The cathodic diaphragm becomes covered with a coat of slimy, purplish-grey or greenish precipitate, which eventually grows through the protecting screen and may be periodically removed therefrom by scrapers, without interrupting the work of the cell, which thus continuously produces the mixed hydroxides.

The precipitated mixture of chromium and zinc hydroxides prepared in accordance with either of the foregoing examples may be washed, thickened by filtering or pressing, shaped into pellets or beads, dried, heated in a reducing atmosphere, and used as the catalyst in the synthesis of methanol from a mixture of carbon monoxide and hydrogen.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the manufacture of chemical compounds by methods involving catalysis by means of metal oxides or hydroxides, catalysing the reactions by means of the metal oxides or hydroxides prepared by electrolysing solutions of the corresponding metal salts.

2. Process for the production of methyl alcohol, which comprises subjecting gases containing carbon monoxide and hydrogen, to the action of catalytic agents consisting of or containing metal oxides or hydroxides prepared by electrolysing solutions of the corresponding metal salts.

3. Process according to claim 2 wherein the catalytic agent comprises zinc oxide or hydroxide with or without chromium oxide or hydroxide, the oxides or hydroxides being prepared by electrolysing solutions of the corresponding metal salts.

4. Process according to claim 3 wherein the catalytic agent contains 3 to 4 atoms of zinc to one atom of chromium.

5. Process according to claim 4 wherein the catalytic agent is substantially free from alkali metal compounds.

6. Process according to any of the preceding claims wherein the metal oxides or hydroxides are prepared by electrolysing the metal salt solutions under an electromotive force in excess of that required to deposit metal.

7. Process according to claim 6 wherein the electromotive force is above 20 volts.

8. Catalysing the formation of methyl alcohol from carbon monoxide and hydrogen, substantially as described.

sisting of electrolysed metal salt solution with metal oxide or hydroxide in suspension, may be passed to a single settling tank, and the supernatant liquid then passed through a cooling device and redistributed to the various cells, if necessary after adjustment of metal salt content.

For operating in parallel a bank of cells may very advantageously be made up from a number of plates of insulating material spaced apart by U shaped members of similar material, the whole being clamped together after the manner of the plates of a filter press. Each U shaped member may be provided with overflow spout or pipe near the upper end of one arm, and a tube may pass through the lower part for attachment, on the inside of the U member to a filter cloth bag surrounding the anode. By means of this tube the acid appearing at the anode may be withdrawn as required. Each cell may be provided with a tube, dipping almost to the bottom, for the admission of the salt solution. In the cells the electrodes may be supported by means of lugs formed thereon and adapted to rest on the upper ends of the U shaped distance pieces forming the bottom and end wall of each cell.

EXAMPLE 2.

A cell of glass or ebonite is divided into three compartments by two diaphragms of closely woven linen fabric, the middle compartment being of larger capacity than the two outer ones. In one of the outer compartments the anode, consisting of a magnetite plate, is suspended. A slow stream of water is admitted at the bottom of this compartment, and an overflow is provided. The other outer compartment contains a sheet of zinc which serves as the cathode. In the middle compartment a screen of wide-mesh fabric is adjusted at a short distance from the cathodic diaphragm, so as to protect the coating of metal hydroxide nearest to the diaphragm from any mechanical disturbance.

The whole cell is filled with water. Some sodium carbonate, e.g. 0.1% is added to the cathodic liquid, and a suspension of colloidal zinc hydroxide and chromic hydroxide to the middle compartment, where it is kept in suspension by bubbling air through or by an agitator. Direct current of 120 volts is applied to the cell, which causes the suspended particles to adhere to the cathodic diaphragm. When a coat of sufficient density has been formed, a solution of zinc nitrate and chromium nitrate, containing 3 to 4 atoms of zinc for 1 atom of chromium, is admitted into the middle compartment at such a rate that a current density at the cathode of about 2 amps. per square dm. is maintained. The temperature of the solution may be controlled so that it is maintained at or slightly above that of the atmosphere. The cathodic diaphragm becomes covered with a coat of slimy, purplish-grey or greenish precipitate, which eventually grows through the protecting screen and may be periodically removed therefrom by scrapers, without interrupting the work of the cell, which thus continuously produces the mixed hydroxides.

The precipitated mixture of chromium and zinc hydroxides prepared in accordance with either of the foregoing examples may be washed, thickened by filtering or pressing, shaped into pellets or beads, dried, heated in a reducing atmosphere, and used as the catalyst in the synthesis of methanol from a mixture of carbon monoxide and hydrogen.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the manufacture of chemical compounds by methods involving catalysis by means of metal oxides or hydroxides, catalysing the reactions by means of the metal oxides or hydroxides prepared by electrolysing solutions of the corresponding metal salts.

2. Process for the production of methyl alcohol, which comprises subjecting gases containing carbon monoxide and hydrogen, to the action of catalytic agents consisting of or containing metal oxides or hydroxides prepared by electrolysing solutions of the corresponding metal salts.

3. Process according to claim 2 wherein the catalytic agent comprises zinc oxide or hydroxide with or without chromium oxide or hydroxide, the oxides or hydroxides being prepared by electrolysing solutions of the corresponding metal salts.

4. Process according to claim 3 wherein the catalytic agent contains 3 to 4 atoms of zinc to one atom of chromium.

5. Process according to claim 4 wherein the catalytic agent is substantially free from alkali metal compounds.

6. Process according to any of the preceding claims wherein the metal oxides or hydroxides are prepared by electrolysing the metal salt solutions under an electromotive force in excess of that required to deposit metal.

7. Process according to claim 6 wherein the electromotive force is above 20 volts.

8. Catalysing the formation of methyl alcohol from carbon monoxide and hydrogen, substantially as described.

Dated this 18th day of July, 1930.

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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 123A.—125/6/1931.]