PATENT SPECIFICATION

640,455

Date of Application and filing Complete Specification: Feb. 20, 1947.
Nos. 5031/47 and 5032/47.
Application made in United States of America on March 4, 1946.
Application made in United States of America on Nov. 25, 1946.
Complete Specification Published: July 19, 1950.

2764

Index at acceptance:—Class 1(i), F3b1.

COMPLETE SPECIFICATION

Improvements in Catalytic Contact Masses

I, OTTO REITLINGER, of 101, 80th Road, Kew Gardens, Queens, in the County of Queens and State of New York, United States of America, 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:—

The present invention relates to the structure of catalytic contact masses. The activity of a contact mass is determined by:—

(1) The degree to which the energy of activation necessary for causing a given reaction is reduced by the catalytically acting substance. This activating property, which depends on the chemical nature of the compound or compounds to be used as catalysts, determines the course of the reaction;

(2) Its efficiency, which is defined as the amount of employed compounds which react at a given temperature and a given pressure per unit of volume of reactor space filled with the catalytic mass, and per unit of time. This latter property is controlled by the physical structure of the contact mass, and can be changed and improved.

The primary object of this invention is to provide contact masses of improved efficiency, —(as defined under 2)—, and methods for preparing same.

The application of non-volatile catalysts in powder form for heterogeneous reactions suffers from the severe disadvantage that powders clog the reactor space and inhibit the homogeneous passage of gases and liquids through the reactor. The following methods have been described for obviating these difficulties:—

(1) The method of fluid catalysis. This method is confined to rugged catalysts and also is restricted as to the size of the particles. Furthermore the difficulties of separating the catalyst particles from the reacting gases increase with decreasing size of the particles.

(2) Mixing the catalysts in powder form with inorganic fibres such as glass, wool, asbestos, mineral wool, and the like, whereby the difficulties arise of reproducing the same efficiency in different batches of the catalytic mass, and also of obtaining in this way a completely homogeneous efficiency of the catalyst per unit volume throughout the reactor. Electro-microscope pictures of such catalytic masses (J. Turkevich, Journ. of Chem. Physics, vol 13, 1945, p. 238) reveal that a small fraction only of the surface of such inorganic fibre masses is covered with the catalyst and a large portion of the free reactor space is bare of catalyst powder.

(3) Compounding the powder of the catalyst into shapes with or without subsequent sintering.—By pelleting such powders the pores and the voids in between the particles are reduced, and the time necessary for the gases to diffuse through these pores is increased and the necessary space velocity decreased, which is equal to reducing the yield that can be obtained at a given space velocity. Also a method of employing relatively low pressures for moulding such bodies from powders as was recently described, cannot prevent such undesirable reduction of the active space and of the size of the pores. By admixing inactive ingredients to the powders of catalytically active substances the active part of the internal surface is substantially reduced, thus reducing the efficiency.

By my invention a novel structure of the contact mass is provided which maintains the advantages of a powdery catalyst without having the aforesaid disadvantages. The novel contact mass is composed of an individual carrier or carriers to which is firmly bonded a homogeneous surface multi-layer completely covering the carriers, and consisting of coherent particles of the catalytic powder. This surface multi-layer is formed by the discrete coherent particles of the catalytically active powder immobilized in a stable packing arrangement the size of the pores

[*Pric*

Pri

formed by the interstices between the particles being of essentially the same order of magnitude as would be presented by a layer of loose particles of the same powder.

The invention consists in a method of bonding a powdery catalyst in a plurality of porous layers to the surface of the carrier elements of a contact mass, comprising the steps of combining with, or applying to, a preferably porous metallic or non-metallic carrier, a metal compound bonding substance, capable of adsorbing water vapour and/or organic vapours, drying, treating said dry carrier with a catalytic agent, for instance a metal oxide or a mixture of metal oxides and/or metals, in powder form, containing the same and/or different metal components as the metal compound bonding substance, in an atmosphere containing, or saturated with, or super-saturated with water vapour, and/or with organic vapours capable of being adsorbed by the bonding substance and by the catalytic powder or applying to said dried carrier to which the bonding substance has been applied a firmly adherent powdery multi-layer surface of catalytically active metal compound in the form of loose particles in the presence of an amount of water and/or organic liquids so limited as to be completely adsorbed by said layer-forming compounds without affecting the powdery packing of said particles, and continuing said treatment until the carrier is completely and firmly covered with a multi-layer of said powder.

The invention also consists in a method as set forth in the preceding paragraph wherein the dried carrier to which the bonding substance has been applied is itself a catalytic contact mass, the efficiency thereof being improved by the subsequent treatment with an additional catalytic agent in powder form.

The invention also consists in the improved catalytic contact masses prepared by the method.

According to my process very fine powder particles are assembled in a plurality of layers enveloping the carriers to the surface of which the innermost layers are bonded only by the adhesive forces of the water vapours or vapours of organic substances which are adsorbed by the substance with which the carriers are pre-treated and by the powder particles from which the powder multi-layers are assembled during the state of their formation.

The critical features of this process are: the exclusion of any pressure, and the exclusion of any adhesive or flux for assembling said powder multi-layers.

The advantages of the use of said powder multi-layers for catalytic reactions are:—

a) The magnitude of the size of the openings of the macro-pores of the catalytic powder multi-layer can be selected by choosing the size of the powder particles. The thus pre-determinable size of the opening of the macro-pores can be arranged to be in the range of the mean free path of the molecules of the reacting gases under the conditions of the reaction. These are the optimum conditions because if the openings of the macro-pores are smaller, the diffusion of the reactants into these pores and the diffusion of the reaction products out of these pores is impaired while the gas flow passes along these powder multi-layers. *Vice versa*, if the openings of the macro-pores are larger than this minimum size the inner active surface of the powder layer, formed by the surface of the pores, is unnecessarily reduced.

b) The surface of the walls of the macro-pores of the powder multi-layers, formed by the individual powder particles, and of the micro-pores of these multi-layers, which micro-pores are contained in the individual powder particles, is formed only by active material, and is not interspersed with inactive or less active zones of any adhesive or flux. Therefore, whereever the molecules of the reacting gases contact this inner surface of said powder multi-layers they can react.

c) The exclusion of any adhesive or flux for assembling and forming the multi-layers precludes the clogging of the pores and the entering of inactive material into said pores by adsorption.

d) By this arrangement the catalytic efficiency of catalytic substances is increased many times,—for the same reaction, and under the same conditions of reaction—, over the efficiency of the same substances prepared by any of the methods hitherto known.

The increase in efficiency of these new contact masses is caused by their ability to allow the gases to diffuse freely throughout the powder layers,—and the formation of these layers depends on the ability of the powder particles and of the substance with which the carriers are pre-treated to adsorb vapours, causing the cohesion of the powder particles and the adhesion of the innermost layers of same to the support to which an intermediate layer is applied which adsorbs the same vapours.

Thus, the formation of these powder multi-layers is closely related to the capability of the constituents from which the powder particles are formed, and of the substance with which the carriers are pre-treated, to adsorb vapours.

As a filling of a reactor for the calytic activation of chemical reactions in fluids, the described contact mass forms three systems of intercommunicating channels of widely differing magnitude and therefore for completely differing purposes. The first system is a lattice or network of communicating channels formed by the individual aggregates and serves to control the hydrostatic conditions for the regular and homogeneous flow of the fluids through said reactor. The second system is a lattice or network of communicating channels formed by the individual powder particles of the powder multi-layers. These channels are the interstices between the individual powder particles and are the macro-pores of the powder multi-layers. The mean diameter of these macro-pores is arranged to be at least of the magnitude of the mean free path of the molecules of the gases under the conditions of the reaction. The channels of the second system,—which are the macro-pores of the powder multi-layers —, communicate with the channels of the first lattice and serve for the diffusion of the gases throughout the powder multi-layers. The channels of the third system are the micro-pores in the individual powder particles. They open into the macro-pores of the powder multi-layers, and serve for the adsorption of the gases or vapours and for the catalytic activation of chemical reactions.

In carrying out the invention, a porous granular support of non-metallic or metallic carrier material is impregnated with a hydrophilic metal compound, forming a bonding or ground layer. To the surface of the impregnated support is applied a porous powder multi-layer consisting of discrete coherent particles of a hydrophilic metal compound which may be the same or a different metal to the metal compound with which the carrier material is impregnated. The powder particles of this porous powder multilayer adhere firmly to, and cover completely, the impregnated carriers. This surface multi-layer is applied to the impregnated cores in the form of diminutive particles giving the surface layer of porous structure, the mechanical strength of which is increased, if necessary, by causing the powder particles to cohere or to bake together by heat treatment.

In the specification, the term "hydrophilic" has been used generically to designate compounds, which, because of their chemical properties or their specific physical structure, adsorb not only water vapour but also other vapours from the surrounding atmosphere; it is well known in the art of adsorption that practically all substances and structures which adsorb water vapour adsorb organic vapours as well.

It is not possible to obtain a uniform coherent surface layer, as defined hereinbefore, upon a porous carrier by merely coating or impregnating the carrier with the catalytic material. If the carrier, even in a moist state, is treated with the catalyst in powder form, the powder does not adhere to the carrier so firmly as to form a homogeneous layer. If the carrier is impregnated with a solution or suspension of the catalytic substance and subsequently dried by heating, the coating shrinks and the surface consists more or less of alternating areas formed by the catalyst proper and by the material and the pores of the support. Heretofore, it was even presumed such a structure of the surface of a contact mass was particularly efficient (c.f e.g. the book "Catalysis" by Berkman, Morrel and Egloff, 1940, pp. 456—482 where the favourable influence of the pores of the carrier material upon the efficiency of the catalyst is described).

In order to obtain a coherent and homogeneous layer of a catalytic powder upon a carrier, it is necessary to increase the adhesion of the catalytic material to the support. According to this invention, this increased adhesion is obtained by a suitable pre-treatment of the support, for instance by impregnating it with a substance capable of adsorbing water vapour and/or organic vapours or, preferably, by precipitating from a solution an intermediate layer of the catalytic or a similar material upon the support. If subsequently a powder of the catalytic material is applied to the impregnated support according to the process of the invention, it adheres firmly thereto. In this way, a contact mass is formed which, even under the microscope, has a completely uniform and homogeneous appearance and a catalytic efficiency by far superior to contact masses consisting ot the same support and the same catalyst but prepared by impregnation only or by powder coating only.

The impregnating ground layer and the surface layer may consist of ferric oxide. In one or both layers the ferric oxide may be replaced, wholly or in part, by other oxides or mixtures or oxides such as chromium sesquioxide, vanadium sesquioxide, cobalt oxide, thorium oxide, or other oxides of the transition metals known for their catalytic activity. In this way, mixed catalysts are obtained, and depending on the specific metal oxides which are used as catalysts it is possible to predetermine the energy of activation which shall be applied to the reaction. This permits of controlling the degree of oxidation or dehydrogenation at which it is desired to stop the reaction. The efficiency of the catalyst is, however, controlled and determined by the size of the particles of the catalytic powder, by the thickness of the outer layer formed by this powder, and by the size of the grains of the carrier material.

In its broadest form, this method may be defined by the steps of combining with the carriers which may be in the form of grains for example a bonding substance causing the catalytic surface multilayer to adhere to said carriers and subsequently treating said carriers according to the present invention with a catalytic agent in powder form until they are completely and firmly covered with a coherent layer of said powder.

The ordinary contact masses prepared by merely impregnating a carrier with the catalytic agent and drying it show, under the microscope, a chessboard-like surface formed by alternating zones of catalytic and carrier material. These alternating zones correspond to areas of different catalytic efficiency, the reaction being confined to the zones covered by the catalyst.

In contradistinction to these contact masses prepared by impregnation only, the contact masses obtained according to this invention have a coherent porous outer packing arrangement wholly composed of the catalytic agent and not interrupted by inactive areas of the carrier material. The inner and outer surfaces offered to the reacting gases are wholly composed of catalytic material and, therefore, greatly increase the reaction rate.

Cohering, or baking together, of the small powder particles composing the outer layer may, if necessary, be brought about by the action of hydrogen chloride and oxygen at elevated temperatures or by heating only; the best way will depend on the physical and chemical properties of the particular substances that are used for activating the reactions hereinafter described.

When for instance the granules are covered with such substances which are catalysts for the reaction of hydrogen chloride with oxygen, whereby chlorine is formed, the mechanical strength of these active shells can be increased, without substantially reducing the size of the pores and the active inner surface of the active surface layer, by subjecting the granules to the action of hydrogen chloride and oxygen at elevated temperatures.

It appears that the mechanical stability of the surface powder multi-layer at normal temperatures is maintained by the adsorbed vapours of water and/or organic substances by the hydrophilic intermediate impregnation layer, and by the adsorption of these vapours by the internal surface of said surface powder multi-layer, the internal surface of which is formed by the pores or interstices in between the individual catalytic powder particles from which these powder multilayers are formed. In the reactor, the water vapour and/or organic vapours will be desorbed but the powder particles will cohere to each other and adhere to the support when subjected to the elevated temperature; as soon as the granules leave the reactor, they readsorb water vapour and the original state is restored.

I have further discovered that said novel structures of catalytic masses can also be applied with great advantage to the building up and combining of catalytic masses, the catalytic active constituents of which are metals and alloys in the pure state or still containing some other compounds, such as oxides and chlorides and also metals containing carbides or other components affecting and determining their activating quality as defined under 1 above.

The preparation of the novel catalysts and their use will now be described in greater detail by means of the following examples for oxidation, chlorination, dehydrogenation and cyclisation reactions, as well as for addition reactions, for hydration, for hydrogenation and alkylation reactions. The properties and efficiencies of some of the representative ones are illustrated in comparison with the same catalysts of the same chemical composition but prepared according to the previously known methods. All parts are by weight unless otherwise stated. It will be understood that the invention is not limited to those specific embodiments and particular data given since the examples are given primarily for purposes of illustration only.

EXAMPLE I.

Granules of suitable size of any of the known porous carrier materials such as Fuller's earth, silica gel, and the like, but preferably granules of pumice within the range of 20 to [illegible] mesh are allowed to stand in a concentrated aqueous ferric chloride solution for a period of about 24 hours. They are then separated from the remaining ferric chloride solution and dried at a temperature of about 180° C. These grains are filled into a tube through which gaseous ammonia is slowly passed for a period of about one hour. The grains are then brought into concentrated aqueous ammonia and left therein for about 24 hours.

The aqueous ammonia is then decanted and the grains are washed until red litmus paper retains its colour and until the suspended excess of precipitate, of ferric hydroxide has been removed with the wash water, while the ferric hydroxide contained in the pores and upon the surface of the grains is retained therein and thereon. The grains, which are now impregnated with ferric hydroxide, are dried at a temperature of about 200° C. and filled into a reactor tube in which they are subjected, at a temperature of about 490° C. and for a period of about 2 hours, to the action of a gas stream containing about ten parts by volume of air and about four parts by volume of hydrogen chloride. The flow velocity of the gas stream is immaterial; I prefer to apply a space velocity of about 3.25 per minute. The carrier grains may be subjected, before and/or after applying the catalyst metal compound in powder form, to the combined action of hydrogen chloride and oxygen or air at elevated temperature, between 200° C. and 750° C. but preferably between 400° C and 600° C.

After cooling, the contact mass proper is prepared by shaking the impregnated grains with ferric oxide, e.g. in a proportion of 40 parts of ferric oxide to 60 parts of impregnated grains. The ferric oxide is preferably applied in the form of a fine powder, for instance so fine that 95 per cent. pass through a sieve of 325 mesh. The powder is gradually added to the grains in a humid atmosphere, which may be super-saturated with water vapour. In this way, the grains adsorb a certain amount of water and hold the ferric oxide powder firmly upon their surface. If this operation has been properly done, the walls of the shaking vessel should not show more than slight traces of the ferric oxide; the humidity should be controlled in such a way that the finished grains do not leave behind more than scant traces of ferric oxide when sliding over dry glass or smooth paper. This is a good indication that the ferric oxide layer adheres sufficiently to the pumice supports. Microscopic observation of the grains shows that they are completely covered with a dense, velvet-like layer and do not show any free spots; each grain presents on its surface the aspect of a sponge; the small particles of the ferric oxide powder forming the innumerable walls thereof.

145.5 grams of the above specific mass, containing about 58 per cent. of impregnated pumice grains, about 39 per cent. of ferric oxide applied in powder form, and about 3 per cent of water, are loaded into a vertical glass tube of 26.5 mm. I. D. over a length of 294 mm. The part of the tube above the contact mass is filled with small pieces of stoneware over a length of about 235 mm. and serves as a preheater.

The reactor is heated as a temperature of about 490° C. and the preheater is brought to a temperature of about 440° C. After passing a gas mixture containing about 10 parts by volume of air and about 4 parts by volume of hydrogen chloride through the tube for a period of about 2 hours, the reactor is ready and fit to be used for oxidation, chlorination or other processes.

EXAMPLE II.

Table I shows the results of various runs made in the reactor and with the contact mass described in Example I, for the chlorination of methane by means of hydrogen chloride and oxygen in air according to the reaction.

$$CH_4 + x\,HCl + x/2\,O_2 = CH_{4-x}\,Cl_x + x\,H_2O$$

wherein x stands for any integer from 1 to 4.

TABLE I.

Gas mixture by volume: $CH_4 : HCl : Air = 4:4:10$

Run No.	Temperature Reactor	Temperature Preheater	Flow Velocity	Space Velocity	Percentage Yield HCl basis	Percentage Yield CH_4 basis
A	491° C.	400° C.	385 cc/min	2.46	69.39	43.43
B	491° C.	400° C.	507 cc/min	3.24	69.72	43.63
C	491° C.	430° C.	507 cc/min	3.24	70.47	44.11
D	491° C.	440° C.	651 cc/min	4.16	67.86	43.77

The chlorinated end product consists of about 38.10 per cent. of methyl chloride, 40.20 per cent. of methylene-chloride, 18.45 per cent, of chloroform, and 3.25 per cent. of carbon tetrachloride. The table shows a uniform and very high conversion of 68 to 70 per cent. with respect to the hydrogen chloride and of about 44 per cent. with respect to the methane.

Whereas Table I shows the results obtained with the novel contact mass, Table II gives the results of control tests made with the same reactor, for the same reaction, under exactly the same experimental conditions, and with the same chemical compound, ferric oxide, as a catalyst. The ferric oxide was used as such or precipitated on various porour carriers in accordance with standard methods of preparation.

TABLE II.

Gas mixture by volume: $CH_4 : HCl : Air = 4 : 4 : 10$

Run No.	Temperature		Flow Velocity	Contact Mass	Percentage Yield	
	Reactor	Preheater			HCl basis	CH_4 basis
G	491° C.	391° C.	469 cc/min	Fe_2O_3 powder on pumice (mesh 60) prepared by shaking in humid atmosphere	8.05	4.3
H.	491° C.	400° C.	505 cc/min	Fuller's earth (mesh 40) impregnated with Fe_2O_3	.83	.45
I	491° C.	391° C.	506 cc/min	Fe_3O_2 Hematite crystals (mesh 20)	5.98	3.2
J	491° C.	391° C.	379 cc/min	Fe_2O_3 amorphous mineral grains (mesh 20 to 60)	1.14	.6
K	491° C.	400° C.	513 cc/min	Grains of pumice (mesh 20 to 60) impregnated with Fe_2O_3	10.0	5.0
L	491° C.	400° C.	507 cc/min	Silica Gel (mesh 14 to 20) impregnated with Fe_2O_3	5.0	2.5
M	487° C	400° C.	123 cc/min	Fe_2O_3 powder on pumice (mesh 80 to 120) prepared by shaking in humid atmosphere	16.05	8.2

In runs H, K and L, the impregnation of the supports was carried out in the same way as described in the first part of Example I but without shaking the impregnated grains with the ferric oxide powder.

A comparison of Table I and Table II shows that pumice grains impregnated with ferric oxide according to known methods convert 10 per cent. of the hydrogen chloride (run K) whereas the novel catalyst, under exactly the same conditions, brings about a conversion of 68 to 70 per cent. (runs A—D).

Table II shows further that the same poor results were obtained by using ferric oxide without a carrier (runs I, J) or by applying ferric oxide powder to an unimpregnated carrier (run G). Even when in the latter case the chlorination is carried out at very low and uneconomic gas velocities (run M) the yields are less than a fourth of those obtained with the new catalyst at normal velocities.

EXAMPLE III.

Table III shows the results of two runs made for the chlorination of ethylene by means of hydrogen chloride and oxygen or air according to the reaction:—

$$C_2H_4 + xHCl + x/2\ O_2 = C_2H_{4-x}Cl_x + xH_2O$$

wherein x stands for any integer from 1 to 4. The runs were made with the same catalyst material and in the same reactor as the runs of Table I.

TABLE III.

Run No.	Temperature		Flow Velocity	Space Velocity	Gas mixture by vol. $C_2H_4 : HCl : Air$	Percentage Yield	
	Reactor	Preheater				HCl basis	C_2H_4 basis
E	491° C.	440° C.	510 cc/min	3.26	4 : 4 : 10	66.7	36.0
F	491° C.	440° C.	452 cc/min	2.9	2 : 4 : 10	56.65	52.73

In run E, the chlorinated end product consists of 30.50 per cent. vinyl chloride, 27.50 per cent. dichloroethylene, 37.70 per cent. trichlorethylene, and 4.30 per cent. tetrachloroethylene for run F, the corresponding figures are 30.65, 29.20, 30.65 and 9.50 per cent.

If the catalysts of Table II are used, hardly 10 per cent. of the hydrogen chloride can be converted to chlorinated olefines whereas under the same conditions the novel catalyst brings about a conversion of 66.76 per cent. for equal parts by volume of hydrogen chloride and ethylene and of 56.65 per cent. for a ratio of ethylene to hydrogen chloride of 2:4.

The chlorination of saturated or

unsaturated aliphatic hydrocarbons and the composition of the chlorinated products is controlled by the nature of the hydrocarbon and the ratio between hydrogen chloride and hydrocarbon introduced into the reactor. The greater this ratio is, the greater will be the proportion of higher chlorinated hydrocarbons in the end product. The novel structure for contact masses can also be used with advantage for the chlorination of other than aliphatic hydrocarbons. The chlorination of benzene, for instance, is readily obtained in this way, and the hydrogen chloride is wholly combined with the benzene to form chloro-substitution products of benzene when a sufficient excess of benzene is used.

Chlorination is only a specific case of the general group of oxidation reactions. The novel catalyst can, therefore, be used generally for oxidation reactions in the gaseous phase. In many cases where the known oxidation catalysts were not active or efficient enough for industrial application, it can be expected that with the aid of the new catalysts prepared according to this invention the reactions will be carried out on a commercial scale. The novel catalysts can, for instance, be employed for the oxidation of hydro-carbons or for the ring formation from paraffins, i.e. benzene from hexane or toluene from heptane.

Though the new catalyst and the method of preparing it has been illustrated by the example of ferric oxide, other metal oxides or metal compounds may be used and prepared in the same way, either for both or only for one or the surface layers upon the carrier material. Grains of a porous carrier are first impregnated with ferric oxide as described above and then shaken with another metal oxide in powder form, for instance with chromium or manganese sesqui-oxide, or *vice versa*; in this way, mixed catalysts of high efficiency and specific activity are obtained.

The contact masses described hereinbefore are particularly useful with respect to the oxidation of organic compounds when it is desired to prepare certain oxidation products with the exclusion of other, as for instance in the oxidation of toluene to benzaldehyde with vanadium oxide as a catalyst.

It is also possible to prepare mixed catalysts by applying to the impregnated granules of the carrier a mixture of powders of suitable metal oxides. These powders may be prepared either by merely mixing the powders of different metal oxides or by co-precipitating different metal oxides and subsequently converting the precipitate to a powder. A mixture of the powders of chromium and molybdenum sesqui-oxides is suitable for the dehydrogenation and cyclization of heptane to toluene.

Oxidation and chlorination reactions are strongly exothermic. Thus usual carrier material for catalysts has a very low thermal conductivity; it is, therefore, often difficult to maintain the optimum temperature for a catalytic reaction within the contact mass and to avoid local overheating and decompositions of the reaction products. This drawback can be obviated by using a porous metallic carrier material of high thermal conductivity.

A metal carrier must be used which—under the conditions of the reaction—does not reduce the metal oxide which is used as the catalyst, to the next lower oxidation stage. Therefore, bronze is suitable as a carrier for chromium sesquioxide but not for ferric oxide.

The surface of the porous metal carrier must be pre-treated by impregnation in the same way as described above for non-metallic carriers in order to obtain a firmly adhering surface layer of the powdered metal oxide or other catalytic compound. Porous metals as produced for various technical applications by sintering metal powder are a suitable carrier material.

EXAMPLE IV.

The addition reaction of ethylene and hydrogen chloride to form ethyl chloride.

$$C_2H_4 + HCl = C_2H_5Cl$$

145.5 grams of the contact mass, prepared according to Example I, containing about 60 per cent. of impregnated pumice grains and about 40 per cent. of ferric oxide applied in powder form, are loaded into vertical tube of 26.5 mm. I. D. over a length of 294 mm.

The steps of subjecting the impregnation layer and the surface layer to the action of hydrogen chloride and oxygen, as described in the Example I, are optional and may be dispensed with. If, however, these two steps are carried out, the grains before serving as catalysts for this reaction, have to be freed of chlorine which has been taken up e.g. in the form of a ferric oxychloride. A stream of oxygen or air is passed over the grains at about 490° C. until the leaving gases do not contain any more chlorine. This step can be shortened by admixing methane or another suitable hydrocarbon in the stream of air.

A gas stream of about 500 cc. per minute of dry ethylene and dry hydrogen chloride is passed through the tube at atmospheric pressure. The employed gas mixture is by volume: $C_2H_4:HCl=1:1.1$. The gases enter the reactor at room temperature, i.e. at about 25° C. and care has to be taken that the internal temperature in the centre of the reactor does not rise substantially over about 60° C. The resulting ethyl chloride is separated from the exit gases in known manner. The conversion rate on the basis of ethylene is about 95 per cent.

Control tests were made with the same reactor, for the same reaction, under exactly the same experimental conditions, and with the same chemical compound, ferric oxide, as a catalyst. The impregnation of the supports was carried out in the same way as described in Example I but without applying the surface layer of ferric oxide powder to the impregnated grains.

Hardly a 15 per cent. conversion rate on the basis of ethylene could be obtained.

Example V.

For the addition reaction of acetylene and hydrogen chloride.

$$C_2H_2+HCl=C_2H_3Cl$$

to form vinyl chloride at about 250° C., the following contact mass is used with advantage. Granules of suitable size of any of the known porous carrier materials such as Fuller's earth, silica gel, and the like, but preferably granules of pumice within the range of 20 to 60 mesh are impregnated with, cupric chloride, dried and then agitated with a fine powder consisting of about two parts of calcium chloride and one part of barium chloride. Calcium chloride is delinquescent and contains sufficient adsorbed water to obviate the necessity of the presence of additional water vapour in the atmosphere in which the impregnated grains are agitated with the powder mixture of calcium chloride and barium chloride. The advantage of this new contact resides in the fact that it allows to obtain good results without the admixture of mercuric chloride to the catalyst; vinyl chloride obtained over mercuric chloride contact masses always contains traces of that compound, which have to be removed.

Example VI.

Preparation of acetone from acetylene and steam according to the equation:—

$$2\,C_2H_2+3\,H_2O=CH_3COCH_3+2\,H_2+CO_2$$

Grains of pumice of the size within the range of 20 to 60 mesh which previously have been provided with an impregnating inner ground layer of ferric oxide as described in Example I are provided with a surface layer by agitating them with a fine powder consisting of about equal parts of ferric oxide and zinc oxide in the presence of water vapour which preferably is supersaturated. About 45 parts of said ferric oxide-zinc oxide powder are gradually applied to about 55 parts of the impregnated grains. The same vertical reactor as described in Example I is loaded over a length of 300 mm. and is brought to a temperature of about 740° C.—12 litre per hour of acetylene and about 15 grams of steam per hour are passed at this temperature through the reactor. From the condensate of the exit gases consisting of aqueous acetone, with traces of acetic acid, and acetaldehyde, acetone is separated by liquid/liquid extraction, to be stripped from the solvent by subsequent distillation. The yield of acetone on the basis of acetylene is about 60 per cent.

Control tests made with porous grains provided either with an impregnating ground layer only consisting of ferric oxide and zinc oxide or with a surface layer only consisting of the said compounds, gave as a result hardly a 10 per cent conversion rate on the basis of acetylene.

Example VII.

Hydrogenation of carbon monoxide, (Fischer-Tropsch Process).

As described in Example I of this application, grains of pumice, about half of them within the range of 20 to 40 mesh and half of them within the range of 40 to 60 mesh, are provided with an impregnating inner ground layer of ferric oxide. The material for the surface layer contains about ½% of potassium carbonate, 2½% of cupric oxide, 5% of manganese oxide and 92% of ferric oxide and is a fine powder, for instance so fine that 95% of same pass through a sieve of 325 mesh. This powder is prepared either by merely mixing powdered cupric oxide, manganese oxide, and ferric oxide in above proportions, but preferably by co-precipitating these compounds with potassium hydroxide and subsequently converting the precipitate after washing and drying into powder of 325 mesh. The powder mixture is soaked with an aqueous solution of potassium carbonate containing same in such concentration that the dried powder contains ½% by weight of this alkali. The soaked powder is dried and ground again to the size passing a sieve of mesh 325. The surface layer is applied to the impregnated grains—as described in Example I—by shaking them in a humid atmosphere with the powder mixture. 45 parts of this powder are gradually applied to 55 parts of the impregnated grains. As described in Example I, after the application of the impregnation layer and again after the application of the said surface layer the grains are subjected to the combined action of hydrogen chloride and air at about 490° C. for about two hours. These steps serving to increase the mechanical strength of the surface layer may be dispensed with if such increase of the mechanical strength is not necessary or not desired. If, however, these steps are carried out, the grains have to be freed of chlorine taken up in the form of ferric oxy-chloride and cupric oxy-chloride as described in Example IV.

148 grams of the above described contact mass are loaded into a vertical tube of mild steel of 26.5 mm. I.D. over a length of 300 mm. The reduction of the powdery metal oxide particles to metal is effected by passing through the tube dry carbon monoxide at a rate of 45 litres per hour for 11 hours at about 325° C. If an increase of the mechanical strength of the surface layer is desired, the small iron particles of which it is composed are slightly sintered by passing hydrogen through the tube at about 400° to 500° C., but preferably at about 450° C. this latter operation of sintering should be followed by a second treatment with carbon monoxide at about 325° C.

After reduction of the contact by means of carbon monoxide the temperature is lowered to about 230° C. and a gas mixture containing equal parts by volume of carbon monoxide and hydrogen is passed through the reactor at the rate of 509 cc. per minute, i.e. with a space velocity of 3.25 per minute. During the first 24 hours the contraction (being the percentage difference, between the initial volume of gas introduced and the final volume of gas leaving the reactor) increases gradually to approx. 50 per cent whereupon it remains stable, and the average yield of hydrocarbons amounts to about 130 grams per cubic metre of employed water gas. About 60% of the obtained products are liquid hydrocarbons, about 20% are solid paraffins and the balance consists of hydrocarbons having more than two C-atoms in the molecule.

The reduction described in the present example can also be effected by means of water gas as used for the synthesis, i.e. with a mixture of equal parts by volume of carbon monoxide and hydrogen at a temperature of about 255° C.

Comparable results with an iron catalyst were reported only when using a pressure of 15 atmospheres (U.S. Patent Specification No. 2,257,457), whilst the working condition according to the given example is atmospheric pressure.

According to the specification of the cited United States patent the catalyst was prepared as follows: In a solution, heated to boiling temperature of iron nitrate which contains for instance 50 grams iron per litre, the iron is precipitated, preferably under stirring, by introducing a vigorous stream of ammonia gas. The iron precipitate is separated by filtration and the main part of the ammonium nitrate removed by washing; the last traces escaping during subsequent heating. The washed catalyst is now impregnated with a ½% potassium carbonate, calculated for iron; is dried at 110° C., granulated or compressed, and filled into the catalytic vessel.

When working under atmospheric pressure the highest yield reported, i.e. by the disclosure of U.S. Patent Specification No. 2,369,106 is 53 cc. of oil (about 48 grams) per cubic metre water gas and this with a space velocity of 1.67 per minute only, thus at half the space velocity of the given example.

The catalyst was prepared according to the specification of this patent by co-precipitating iron hydroxide and calcium hydroxide from a solvent solution, drying the precipitated powder and pelleting same, or by impregnating infusorial earth, diatomite powder, etc. with a solution of an iron salt and calcium salt and co-precipitating the hydroxides within and upon these carriers.

Comparable results at atmospheric pressure are reported only with a cobalt-thorium oxide catalyst (Hall & Smith, Journ. Soc. Chem. Ind., 1946, pp. 128—136) and this with a space velocity of 1.09 per minute only, i.e. at one third of the space velocity of this example.

If, however, the cobalt-thorium oxide catalyst is prepared in the same manner as described in this Example VII, the reaction can be carried out at a greater space velocity.

The advantage of the novel structure of contact masses is not only the higher space velocity with which the reaction can be carried out but still a greater advantage for this specific example is the possibility to obtain the same results, or substantially the same results, under atmospheric pressure as were obtained heretofore under pressures of at least 10 atmospheres and higher. Moreover, as this specific reaction is very sensitive to temperature changes the problem of the temperature control for industrial production is not easy to solve when working at pressures of 10 atmospheres and higher.

Hereinbefore, I have described a method for a better control of the temperature for catalytic oxidation and chlorination reactions, which consists in the use of a porous metallic carrier of high thermal conductivity instead of employing the usual porous carrier materials for catalysts having a very low thermal conductivity.

The elimination for the use of porous metallic carrier materials for catalysts the catalytically active constituents of which are metal oxides stated for oxidation reactions has to be reversed for catalysts the active constituents of which are metals, and for hydrogenation or reduction reactions and may be stated as follows:—

A metal carrier must be used which does not oxidise the metal which is used as the catalyst under the conditions of the reaction to its lowest oxidation stage.

Porous iron granules are a suitable carrier material for the iron powder catalyst for hydrogenation reactions.

EXAMPLE VIII.

Hydrogenation of carbon monoxide.

Turnings of porous iron as obtained by any one of the known metallurgical processes and sufficiently disintegrated, for example, to the size given in example VII, within the range of 20 to 60 mesh, are provided with an impregnating ground layer of ferrous oxide, as described in Example I, but without subjecting the impregnated turnings to the combined action of hydrogen chloride and air at elevated temperature. Then a surface layer is applied to the impregnated porous metallic grains by shaking them in a humid atmosphere with the same powder as described in Example VII. The last step of subjecting the grains after the application of the surface layer to the combined action of hydrogen chloride and air at elevated temperature takes very short time if porous iron is the carrier, the surface layer of ferric oxide being very quickly converted into ferrosic oxide; the entering hydrogen chloride air mixture is pre-heated to a temperature of at least 400° C. and the reactor is heated to a temperature of at least 450° C., preferably to about 490° C.

166 cc. of the above described contact mass are loaded into a vertical tube as described in Example VII; if the same initial reduction and induction steps are made, practically the same results are obtained as described in Example VII, and the temperature gradient between the centre and the wall of the reactor is small.

Similar contact masses are also prepared with success by applying the active surface layer in the form of a metal powder to the impregnated cores of porous metals. Instead of reducing the ferric oxide powder after the formation of the porous surface layer, powdered iron itself is used immediately after it has been obtained by reduction of the oxide by means of hydrogen and is applied to the impregnated porous iron cores in an inert humid atmosphere, consisting for example of hydrogen, nitrogen or carbon dioxide containing water vapour. In an essentially analogous manner iron powder, prepared from iron carbonyl, can be applied.

It is know that for the synthesis of ammonia an iron catalyst is used which contains aluminium oxide or potassium oxide, or both of these compounds. Therefore, if it is desired to apply my novel structure of iron catalysts for the ammonia synthesis, the same porous iron turnings disintegrated to the size within the range of 20 to 40 mesh as described in Example VIII are used. These porous iron grains are provided with the same impregnating inner ground layer of ferrous oxide as described in Example VIII. The composition of the surface multi-layer differs, however, slightly. For example, the material for said surface layer contains about 95 per cent. of ferric oxide and about 5% of aluminium oxide, and can be prepared as described in Example VII by merely mixing the powders of said compounds in this proportion, or preferably by coprecipitation of these compounds, conversion of the precipitates, after washing and drying, into a powder of 325 mesh, and subsequently applying the same steps which have been described for the preparation of the iron catalyst with porous iron cores for the hydrogen-carbon monoxide reaction, in Example VIII. The grains coated with ferric oxide or—as the case may be—with ferrosic oxide are loaded into a reactor for the synthesis of ammonia and both the surface and the impregnating ground layer of these grains are reduced in one of the known manners, e.g., by means of hydrogen at the suitable temperatures, preferably between 400° C. and 500° C.

The results obtained by the application of these grains as catalysts are by far superior to those obtained with the iron catalysts prepared by the known methods.

It is known that for the oxidation of ethylene to ethylene oxide, silver oxide is used as catalyst. According to my method a catalyst suitable for this reaction can be obtained by impregnating grains of pumice with silver nitrate, converting it into silver oxide, and subsequently forming a surface layer by shaking the impregnated grains in humid atmosphere with a powder of silver oxide of a size passing a sieve of 325 mesh.

It is known that for dehydration reactions aluminium oxide is used as a catalyst. An aluminium oxide catalyst of high efficiency can be prepared from any porous carrier material. as for example, porous grains of aluminium oxide, by impregnating them with a hydrophilic metal compound, drying and by subsequently applying to the dried, impregnated supports a surface multi-layer of aluminium oxide powder particles. This is done by shaking the impregnated aluminium oxide supports with aluminium oxide powder in the presence of water vapour and/or organic vapours.

The porous carrier material, which may also be of porous or so-called activated aluminium oxide is impregnated with any hydrophilic material; as for example, ferric oxide, cuprous oxide, or chromium sesquioxide, and subsequently hydrated aluminium oxide is applied to these impregnated carriers by shaking them with hydrated aluminium oxide powder in an atmosphere which is saturated or even super-saturated with water vapour and/or with vapours of organic substances which are adsorbed by the impregnating substance and by the aluminium oxide powder.

Other metals or alloys may be used and prepared in the same way, either for both or only for one of the inner impregnating ground layer and the active surface layer upon the carrier material. For example, a nickel or a cobalt catalyst can be prepared by the same method.

The classes of reactions from which above examples were given widely differ from each other, and the same is true of the chemical compounds used as catalysts to bring about these reactions. The common feature, however, is the physical structure of said catalysts, the method to build them up and the resulting improvement of their efficiencies compared with such as obtained by other methods of preparation hitherto known.

Every one skilled in the art can adapt and vary the method of preparation so as to meet the physical and chemical properties of the catalytic active constituents and of the appropriate carrier material. For example, if aluminium chloride, zinc chloride or another deliquescent compound has to be applied as surface layer (aluminium chloride for alkylation, zinc chloride for chloro-methylation) the application of the surface layer to the impregnated grains will be made with close control of the humidity of the atmosphere or even in dry air, depending on the original water content of these deliquescent substances.

It will be understood that, quite as the novel structure of catalytic masses and their novel method of preparation can be employed for the building up of catalytic masses from all solid chemical compounds and from all solid elements, they also can be used for all reactions for which the catalytic active constituents of which they are composed are appropriate, said novel structure increasing many fold the efficiency of the catalytic masses without, of course, exerting any influence upon their activating properties the latter depending on the chemical composition, as outlined under (2) and under (1) in the second paragraph of this disclosure.

Although the examples given hereinbefore are chosen from reactions in the gaseous phase it will be understood that contact masses of the same physical structure can be employed for reactions in the liquid phase. The mechanical strength of the porous surface layer can be increased in conformity to the greater requirements for said mechanical strength of a porous material which has to resist the flow of liquids, by sintering or cohering as stated above. By choosing a coarser powder for the surface layer the size of the pores of the active surface can be increased so as to take into account the greater viscosity of liquids since the size of the pores of the surface layer depends on the size of the powder particles from which it is built up.

It is obvious that the method of preparing the novel structure of contact masses may be varied to a considerable degree in many respects without departing from the scope of the invention.

For example:—

The efficiency of the new contact masses can be further improved by increasing the thickness of the active surface layer by repeating the steps by which it is produced.

In the treatment of the impregnated grains with the catalytic powder for the application of the active surface layer water vapour can be replaced by vapours of compounds which are adsorbed by the powder of the catalytic substance which is used as the active surface layer and by the substance which is employed for the inner bonding layer. As a rule vapours of substances having some polar affinity towards both the materials of the surface and of the bonding ground layer are suitable for this purpose, provided however, that the adsorbed vapours can readily be desorbed by heating without formation of carbon black and without even partial decomposition. For example, vapours of ethyl alcohol give quite good results for the preparation of a homogeneous porous surface multi-layer from powder particles of catalytic substances which adsorb these vapours. Similarly suitable are vapours of methyl alcohol. It must, however, be avoided to wet, moisten or sprinkle the impregnated grains or the catalyst powder with the liquid the vapour of which is employed because the powder particles agglomerate irregularly and form small clumps at the spots where the impregnated grains or the catalyst powder are wetted, thus preventing the porous surface layers which have become homogeneous. Surface layers which have become homogeneous in this way causes considerable reduction of the efficiency of the respective catalytic structure.

Instead of preparing the impregnating inner bonding ground layer by impregnating a porous support with a solution of a metal compound, and causing said solution to form a precipitate upon and within said support, the grains of the porous carrier material can be subjected to a gas stream consisting of or containing vapours of metal compounds, e.g., metal chlorides, which will be adsorbed by the porous supports and form an impregnating layer of a metal chloride or chlorides which can be converted or not converted—as the case may be—into metal oxide or oxides.

For example, grains of silica gel are impregnated with anhydrous ferric chloride when subjected to a gas stream containing ferric chloride. The ferric chloride is converted into ferric oxide and the grains thus impregnated with ferric oxide are covered with a surface layer of powdered ferric oxide as described in the given examples.

Aluminium chloride or zinc chloride vapours are adsorbed by porous carriers of alumina, or of silica gel. The resulting impregnating layer is converted into oxide in known manner, or—as the case may be— is used as such and without conversion into oxide as bonding agent for a surface layer consisting of powders of the chlorides or oxides of aforesaid metals.

Carrier bodies to the surface of which the powder particles of the surface layer adhere, can also be prepared by coprecitating the carrier material together with the bonding material.

For example:—

Aluminium oxide can be co-precipitated with ferric oxide, chromium oxide, or with another oxide, washed, dried, sized and pelleted or pilled. Subsequently the active surface layer is applied in the form of powder in order to obtain the results hereinbefore described.

Silica gel and metal oxides can be co-precipitated from a prehydrolized solution of water glass and a solution of metal salts, i.e. silica and ferric hydroxide from prehydrolized water glass and ferric nitrate.

Ethyl ortho silicate is prehydrolized from a solution in ethyl alcohol by the addition of water. The sol immediately turns into gel by the addition of ferric oxide powder, occluding the ferric oxide and forming herewith a net like structure of silica and ferric oxide. This gel, when partially dried and pilled, forms bodies the structure of which resembles the structure of silica gel impregnated with ferric oxide. These bodies can serve as carrier for a subsequent coating with the surface layer of a metal oxide powder.

Quite recently a method was described for the preparation of such bodies by coprecipitation of silica and chromium sesqui-oxide from ethyl ortho silicate in the presence of chromium sesqui-oxide. If such gel infiltrated with chromium sesqui-oxide is partially dried, and pilled, metal oxide can be applied to it as described above, to form a coherent active surface layer the catalytic efficiency of which is many times the efficiency of the pilled gel bodies without said surface layer.

Bodies prepared by precipitating metal oxides in the presence of powdered diatomaceous earth and by compounding the resulting mixture of metal oxides and impregnated diatomaceous earth into pills, are also excellent carriers to which an active surface layer in the form of powder can be applied. In this way the efficiency of the specific Fischer-Tropsch catalyst is substantially improved.

As a rule a substance will be suitable for the formation of the inner layer which is necessary for making the powder particles of the active surface layer adhere to the support, if it does not:—

(a) carbonize during the catalytic reaction;

(b) evaporate under the said conditions;

(c) poison the catalytic surface layer or have any other detrimental influence on the reaction.

For example, if an active surface layer of ferric oxide is used, the bonding material must not contain sulphur in such form as to form iron sulphide with the ferric oxide of the surface layer;

(d) change the stage of oxidation of the compound forming the active surface layer when subjected to the conditions of the reaction. If a metal oxide powder is to be used for oxidation and dehydrogenation reactions said metal oxide powder must not be reduced into its next lower degree of oxidation by the material of the bonding or ground layer. *Vice versa*, if a metal or an alloy powder is to be used for hydrogenation reactions said metal must not be oxidized by the compound forming the bonding or ground layer.

For certain reactions and certain metal oxides phosphoric acid is a suitable bonding material.

(e) exhibit too strong a bonding power in order to avoid adherence of surface layers of adjacent grains to each other;

(f) occlude the individual particles of the powder forming the active surface layer.

For example: Beads of glass or of porcelain, after having been submerged in a solution of barium oxide in absolute methyl alcohol, are made to fall through a current of hot air into a vessel containing the catalytic powder. If the height of the fall is properly adjusted the catalytic powder adheres to the beads, but the adherence of surface layers of adjacent grains to each other is avoided. The thickness of the layer of this first coating with metal oxide powder is increased by further agitating said beads with the metal oxide powder in humid atmosphere. The results with this contact structure, however, are not as good as with the contact structure prepared according to the preferred embodiment described in the given examples.

The term "oxygen" as used throughout the specification and the claims is meant to cover not only oxygen but also oxygen-containing gases, preferably air, and the term "hydrogen chloride" includes hydrogen chloride, moist or dry. All components of the gaseous mixtures may be used pure or mixed with other gases, and the term "mixture of coprecipitates" is meant to cover not only physical mixtures but also solid solutions.

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

1. A method of bonding a powdery catalyst in a plurality of porous layers to the surface of the carrier elements of a contact mass, comprising the steps of combining with, or applying to, a preferably porous, metallic or non-metallic carrier, a metal compound bonding substance, capable of adsorbing water vapour and/or organic vapours, drying, treating said dry carrier with a catalytic agent, for instance a metal oxide or a mixture of metal oxides and/or metals, in powder form, containing the same and/or different metal components as the metal compound bonding substance, in an atmosphere containing, or saturated with, or super-saturated with water vapour, and/or with organic vapours capable of being adsorbed by the bonding substance and by the catalytic powder or applying to said dried carrier to which the bonding substance has been applied a firmly adherent powdery multi-layer surface of catalytically active metal compound in the form of loose particles in the presence of an amount of water and/or organic liquids so limited as to be completely adsorbed by said layer-forming compounds without affecting the powdery packing of said particles, and continuing said treatment until the carrier is completely and firmly covered with a multi-layer of said powder.

2. A method as claimed in Claim 1, comprising the steps of coprecipitating the carrier material and the metal compound bonding substance and shaping the coprecipitate prior to drying and the subsequent treatment with the catalytic powder.

3. A method as claimed in Claim 1, comprising precipitating the metal compond bonding substance upon the carrier from a solution thereof, removing the solvent, and preferably also the excess of precipitate and drying, prior to the subsequent treatment with the catalytic powder.

4. A method as claimed in Claim 3, wherein the carrier consists of a metal which does not reduced the metal compounds of the surface layer when subjected to the conditions of the reaction for which said contact mass is used as a catalyst.

5. A method as claimed in Claim 3, wherein the precipitated metal compound bonding substance and the catalytic powder are essentially metal oxides.

6. A method of preparing a contact mass as claimed in any of the preceding claims, comprising the steps of impregnating the porous carrier elements with the solution of an iron compound, preferably ferric chloride, causing said solution to form upon and within said carrier a precipitate of a ferric compound forming ferric oxide on heating, drying said carrier, and applying in an atmosphere containing, saturated with, or super-saturated with water vapour and/or organic vapours to the surface of said dried impregnated carrier a firmly adherent porous layer of powdery ferric oxide.

7. A method as claimed in Claim 1 wherein the dried carrier to which the bonding substance has been applied is itself a catalytic contact mass, the efficiency thereof being improved by the subsequent treatment with an additional catalytic agent in powder form.

8. A method as claimed in Claims 1 to 7 wherein the dried carrier to which the bonding substance has been applied, is,

before and/or after the application of the catalytic metal compound in powder form subjected to the combined action of hydrogen chloride and oxygen or air at elevated temperatures, between 200° C. and 750° C., but preferably between 400° C. and 600° C.

9. A method as claimed in Claims 1 to 8, wherein the carrier after the catalytic metal compound in powder form has been applied thereon, and after, or without, the subsequent heat treatment in the presence of hydrogen chloride and oxygen, is treated with a reducing agent until said powder particles of the porous surface layer are at least partially reduced to metal.

10. The improved catalytic contact mass when prepared or produced by the methods or processes of manufacture hereinbefore particularly described and ascertained or by their obvious chemical equivalents.

11. The method of preparing a catalytic contact mass substantially as described.

Dated this 20th day of February, 1947.
MARKS & CLERK.

Leamington Spa: Printed for His Majesty's Stationery Office by the Courier Press.—1950.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. 0d. each (inland) 2s. 1d. (abroad) may be obtained.