

March 30, 1937.

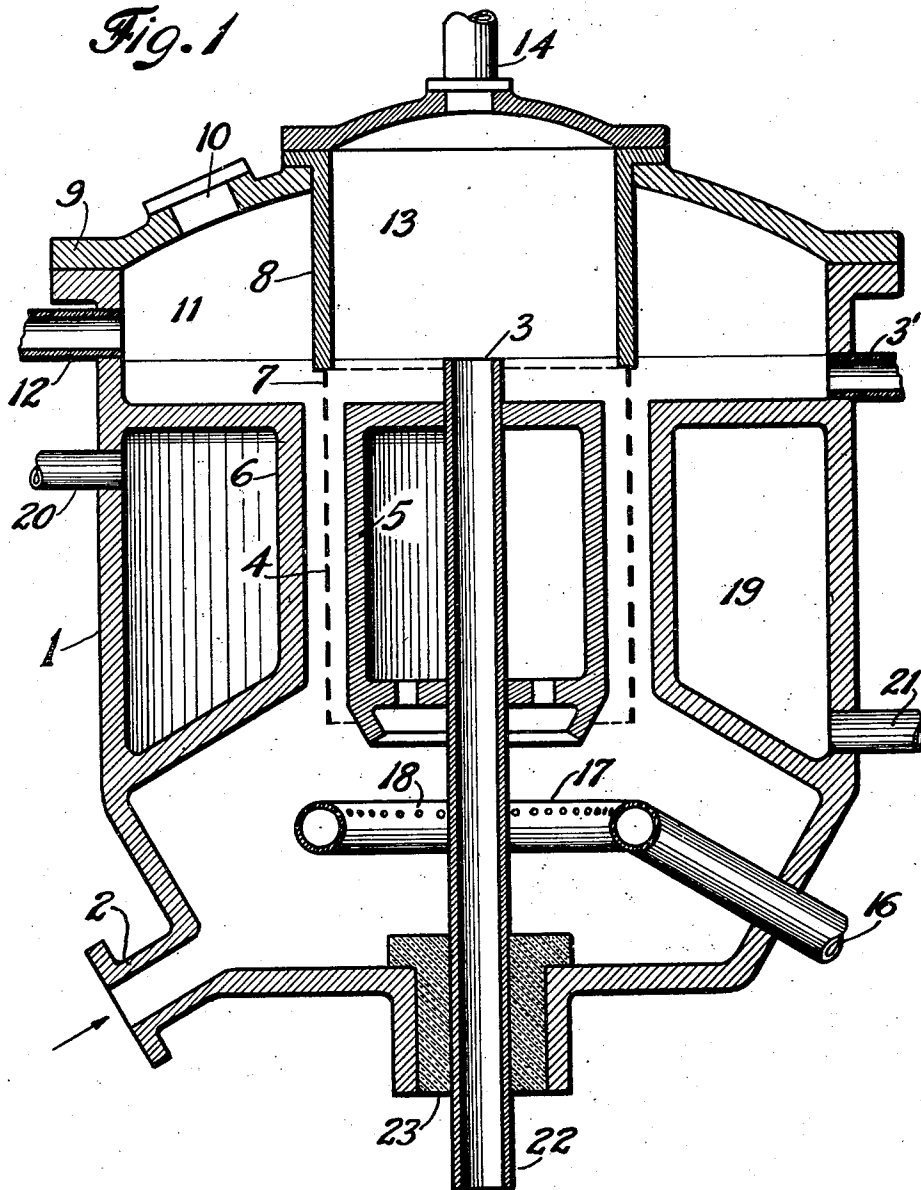
J. F. WAIT

2,075,150

PROCESS FOR THE PRODUCING OF METALS AND UTILIZATION THEREOF

Filed Nov. 7, 1932

2 Sheets-Sheet 1



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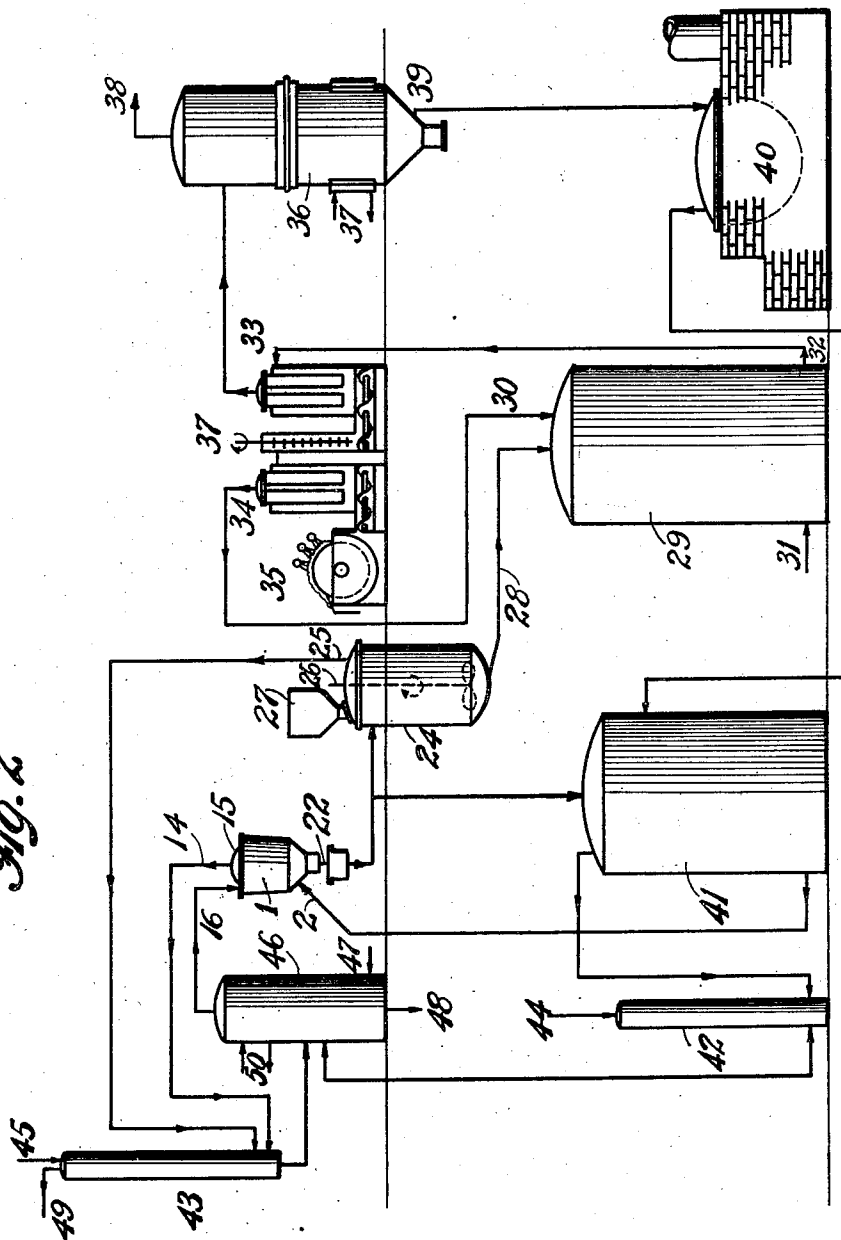
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PROCESS FOR THE PRODUCING OF METALS AND UTILIZATION THEREOF

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2 Sheets-Sheet 2

Fig. 2



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UNITED STATES PATENT OFFICE

2,075,150

PROCESS FOR THE PRODUCING OF METALS
AND UTILIZATION THEREOF

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13 Claims. (Cl. 204—21)

This invention relates chiefly to methods of preparation of alkali metals or solutions of these metals and their compounds in compounds of alkali metals; and the use of such compounds and solutions in fusions as in the manufacture of organic chemicals and for purposes of otherwise promoting or influencing chemical reaction. I have found that by using the methods described herein it is possible to greatly reduce operating hazards and to lower cost of manufacture of alkali metals and compounds thereof, and to decrease the cost of production of organic chemicals whose manufacture or treatment involves the use thereof.

In many chemical processes, mixtures of compounds of alkali metals are used and it is desirable to alter the proportion of the metals involved. Again, as in mixtures of the chloride of the alkali metals it is often desirable to decrease the chloride content. This is done by subjecting the concentrated or fused compounds thereof to electrolysis thus depositing one of the metals such as breaking sodium chloride into its parts and producing metallic sodium, and at times the further conversion of sodium as into sodamide by the action of ammonia or into a hydride as by the action of hydrogen.

By the term fused is meant that state existing when a solid compound is heated to the point where its properties approach those of a liquid, this point usually being near the melting point of the compound involved. The effect of moisture and other foreign products is to alter the fusion point so that it does not equal the true melting point of the pure compound. As a salt or hydroxide containing water is concentrated as by evaporation, it gradually approaches the condition of dehydration which term is applied in the art to the condition of being approximately water free in the sense that most of the water has been removed, as compared with the state of absolute dehydration wherein all of the water has been removed except traces of water which may be in definite chemical or physical equilibrium with the conditions involved.

The process may be used to produce a state of dehydration of compounds of such alkali metals, wherein the water content is decreased or entirely removed by electric power. Relatively cheap electricity is thus substituted for more expensive chemical heating or other means as has been used in the past. As an example of this, the moisture content of a commercially and partially dehydrated chloride of sodium may be removed by electrolysis of the fused mass thus producing a state of complete dehydration. Furthermore, vacuum may be applied to the operation, to assist in carrying off gaseous products of the electrolysis producing the metal. In case where an excess of a dehydrating agent is required, the electrolysis

may be continued past the dehydration point, thus creating an excess of free sodium. In operating a cell continuously for this purpose it is therefore but necessary to discharge both fused chloride and metal as contrasted with the usual method of operation whereby sodium alone is discharged in one system, the isolated metal being later added to a hydroxide or chlorides or mixtures thereof.

As an alternate method of dehydrating the fused material, it is economical to add to the partially dehydrated compound, a mixture or solution of the compound containing free metal or some derivative thereof as, for example, a solution of sodium or sodamide in fused salt of soda. This method eliminates some of the corrosive and hazardous conditions involved in electrolysis of such compounds when mixed with small amounts of water.

In using alkali metals and compounds thereof for the preparation or treatment of chemicals it has been the usual practice to isolate the metal, solidify the same, pack, store and ship the same. Thereafter the metal would again be made fluid and used. This has involved unusual hazards affecting both life and health and has caused a loss in yield due in part to handling and exposure to the elements.

My invention involves the use of a closed system which greatly reduces the hazard and prevents air and other elements from acting in a deleterious manner. It results in less costs of labor, yield and insurance and greatly improves the safety and the health of the operators.

Another feature of the invention is storage and/or use of the alkali metal in relatively dilute solution or suspension in a fluid material such as fused alkali compound or a petroleum product or mixture thereof. The compound itself may react or be a catalyst or merely used as a vehicle. This method of using an inert fluid in combination with an alkali compound which is treated with an alkali metal or a derivative such as an amide or other equivalent dehydrating or reacting substance gives excellent results in organic reactions. It gives with proper mixtures and concentration a control otherwise unattainable, for example, the mixture of selected amounts of chlorides, a hydroxide and free metal may be mixed with a universal oil containing substances to be acted on, the oil in effect being a dispersing medium both regards the alkali and compounds thereof and with regard to the chemical dissolved or suspended within the oil and which chemical may itself be of a normal constituent of oil.

In the electrolysis of fused hydroxides, passage of a gas through the mass assists in removing the products of the reaction. This gas may be or contain vapors of substance to be treated as for example hydrocarbons. Thus an oil with im-

purities may be so passed through the electrolytic or reaction zone. The fused mass or a substance formed therein or withdrawn therefrom may be removed to a separate contact zone. Such features of usable ways of applying the invention are described in my applications Ser. Nos. 612,650, 613,080, 613,081, 613,150, 613,151, 616,071, 627,170 and 627,171. Other features are described in Ser. No. 482,267 and Patent No. 1,913,145 and French Patents Nos. 755,875, 756,203. Equivalent procedure may be established as by freeing an alkali metal or other metal with an unpaired electron and introducing the same into a melt such as one containing chlorides or hydroxides of an alkali metal, thus aluminum for example may be introduced into a near eutectic mixture of sodium and potassium hydroxides and the so formed mixture used for treating a hydrocarbon such as oil. In such connection a solution or colloidal suspension is included within the meaning of the expression "mixture".

Fusions or other reactions carried out in mixtures of compounds of alkali and like metals or in contact therewith have the advantage of greater fluidity of mix and make it possible to operate at a temperature below the melting point of a single compound. Such fusions or reactions may so be carried out with the use of a dehydrating or reacting agent as an alkali metal or other metal with an unpaired electron or a compound thereof. On the recovery of the hydroxides or chlorides from a reaction, it is often desirable to readjust the ratio of the component parts which may be done by electrolysis.

In the operation of the ordinary electrolytic cell such as has been used for the treatment of an alkali metal or compound thereof the material has been charged into the cell in approximately the exact amount required for decomposition. In most instances, the flow of the products has been in a different direction from the natural flow of the material through the cell. I have found numerous advantages in causing a parallel flow of the products of decomposition and the compound charged in excess of that used in decomposition. This includes reduction in the diffusion which is detrimental to high yield and efficiency. It is also possible to so control the feed and the electrolysis as to yield a final product containing the desired percentage of alkali metal or its derivative.

The lowering of the melting point as by use of a mixture of two alkali compounds renders the system more positive and less hazardous. The increased fluidity also makes it possible to operate at lower temperatures than is otherwise possible. In the electrolysis of mixtures of compounds of two metals it is sometimes possible to set free two metals in a proportion depending upon their natural properties and the controlled conditions including current, temperature and velocity.

In usual processes it has been necessary to discard the used salts or hydroxides or for example to recover the hydroxide or chloride component of fusion mixtures by evaporation, filtration, dehydration, etc. My invention provides for the control of conditions such that concentrations may be made of the compound desired in a portion of the hydroxide and the remaining portion of the hydroxide, which is relatively free from the chemical may be readjusted as to its components and again used in a subsequent fusion or other treatment without the expense of dilution concentration and dehydration. My invention also permits the use of components left therein which

would be destroyed if the hydroxide or salt were put through a regular recovery system. Large savings may also be made in those processes where after fusion the alkali content is wasted as by neutralization with an acid.

After the fusion or reaction has been completed for the step organic salts so formed may in some cases be recovered by concentration or nearly complete separation from the fused compound as by filtering. If a fluid material such as a mineral oil is added it may facilitate this separation as by dilution or solvent action. In this case the compound or part thereof may be recovered and received without such a large expense of diluting as is ordinarily resorted to.

In treating a silicious compound of a treating metal such as beryl the same may be rendered suitable for electrolysis as by dissolving in a fused melt for example a eutectic mixture of sodium and potassium hydroxides. Electrolysis at between about 250° C. and 400° C. will release metallic component so that the mixture as discharged in the described manner may be used as for treating oil. The usual temperature of about 600° C. is thus not necessary and operating savings are realized. Such reaction appears to be complex wherefor I offer no explanation of the mechanics of the reaction. Such combination of elements thus involves two paired electrons which may become unpaired and one unpaired and two paired which may yield three unpaired electrons under the conditions of reaction. Other similar combinations such as sodium and calcium or magnesium may be used.

In utilizing chlorides of metals such as sodium the chlorine set free by electrolysis may be utilized as by reaction with an organic substance such as heavy distillate or fixed gases and for purposes of utilizing the chlorine compound as for addition of a radical to hydrocarbon. With such a gas forming compound I prefer that the rate of flow be substantially in excess of about five feet per minute. The free sodium facilitates such reaction and in one manner apparently by forming an intermediary additive compound wherein the chlorinated radical adds to the sodium and this may react as do corresponding magnesium compounds in forming a carbinol or other hydroxy containing compound which may then be further added to as to form an ether. A chlorinated saturated chain compound may be treated with sodium and the organo-sodium chloride then treated with carbon dioxide and dilute acid to form an organic acid. Such and similar reactions are known for a number of metals and I have found that sodium may be used as a substitute for the other metals such as magnesium and zinc.

My invention in some applications involves separation of two elements such as sodium and chlorine and then attachment of the chlorine to a hydrocarbon with subsequent recapture thereof by the sodium. In some instances it is desirable to again electrolyze the so formed chloride and thus repeat the cycle.

Another feasible application is the electrolysis of aqueous chloride to form hydrogen and chlorine and addition of one or both of these gases to hydrocarbon. The hydroxide may be used to treat oil or other hydrocarbon and in aqueous association or in dehydrated form. The dehydrated form may be used as a source of free sodium for treatment of hydrocarbon in isolation or in admixture with the hydroxide. Copending

applications further describe features of this application.

In the electrolysis of a salt of a metal with one unpaired electron such as sodium chloride I have found it generally desirable to add a compound such as potassium chloride and to so give a mass fluid at temperature much below the melting point. By passing the salt through the electrolytic zone at a rate in excess of the rate of electrolytic dissociation it is possible to deliver a mixture of the metal and the compound.

Prior methods have involved the necessity of bailing out or similarly removing the metal. The mixture may be allowed to stand externally to the electrolytic zone that separation may be effected and the molten metal may then be drawn off and the melt returned to the zone. The chlorine gas may be drawn off in the usual manner and its removal from the reaction or liberation zone facilitated by electrolyte passage upwardly across the electrode. Such method may also be used in electrolyzing aqueous chloride to increase the yield and prevent secondary reactions and deterioration of electrodes. Such velocity is preferably in excess of about a few feet per minute.

The invention may so be used for treating mixtures of chlorides of alkali metal or metals and other metallic compounds such as silicates, oxides or hydroxides of alkali metals and/or metals such as beryllium and aluminum. Under some conditions phosphates may so be treated. Flow through the cell may be utilized to release or alter substantial quantities of one or two metals, as beryllium and aluminum while retarding or preventing substances such as sodium chloride from being disassociated or split apart. Similarly sodium may be fed in appreciably greater amounts than potassium in mixtures of sodium and potassium chlorides. Previous efforts to utilize chlorides for preparation of alkali metal have resulted in detrimental operations disadvantageous or fatal to the process and including high maintenance and hazards. By my invention it is feasible to produce a mixture as either solution or suspension or quantities that are equivalent in form. The discharged melt may pass either greater or less in amount in the chlorine chamber and the flow may be zero therefrom. The flow of unelectrolyzed portions may be substantially greater than about twice the flow of electrolyzed portions.

The electrolytic cell may be constructed as previously described and may involve the usual form of electrodes and separating success. The casing may be adapted to have a tightly fitting cover in contrast with prior structure involving loosely fitting covers adaptable to removal on explosion. Direct or unidirectional pulsating current may be applied. Ammonia may be added to the mass containing free metal and sodamide so formed. The resulting solution may be used for indigo fusions. In this manner the temperature is kept substantially the same and the isolation of sodium is not involved. The phenylglycine salt readily reacts and with resulting decrease in cost and increased safety. Hydroxide or other compound may be used or present in the melt to facilitate operation. The production of melt for such reaction may be made continuous to keep approximate pace with continuous fusion, and separation of organic products for subsequent flaking and oxidation. Portions of the melt separated before dilution may be returned to the fusion zone or to the electrolysis zone.

As before suggested, an inert fluid, such as pe-

troleum, or mineral or coal oil may be used in combination with dehydrating or reacting substance used in combination with a melt containing a metal with an unpaired electron. The limits of such usages are from about five percent to about ninety-five percent of the inert fluid as regards the melt when the operation is discontinuous. With continuous operation a small amount of melt may serve a very large quantity of inert fluid which may carry substance to be treated and which fluid facilitates control of the reaction and separation of products of reaction. Organic salts and/or other compounds may be separated from the melt by known means. The use of an inert fluid such as mineral oil or vapors thereof or gaseous substance such as hydrogen-methane mixtures generally facilitate control of reaction and separation. Utilization of a light oil or a gas to assist in volatilization improves treatment of a substance when it is reacted in all or in part in the vapor phase.

Prior methods involving treatment of a fused substance such as alkali chlorides and/or hydroxides involved considerable expense in diluting and as with subsequent concentration thereof. Inert fluid facilitates control to yield more desirable amount or form of products yielded and facilitates separation of fused substance therefrom. Portions of petroleum and other similar hydrocarbons such as that derived from coal tar and vegetable and other oils or derivatives may be so treated. In such instances adequate inert fluid may be associated therewith as parts which will remain substantially inert while active portions will react. Further amounts of inert fluid may be applied as desired.

Methods of preparing metallic sodium have generally involved the well known electrolysis of sodium hydroxide. In a few instances sodium chloride has been electrolyzed but high temperatures have been involved with unusually high operating costs including that of maintenance. Lack of proper fluidity has been involved. I have found that sodium and potassium chlorides may be used in admixture to form a fluid, relatively low melting, mass suitable for electrolysis. By flowing the melt upwardly across the electrodes at appreciable velocity better operation may be realized. Discharge of a mixture of fused chloride and the released metal furnishes better operating conditions. A reacting gas or two such as nitrogen and hydrogen and their resulting combination, ammonia, may be placed within or close to the zone of electrolysis. Thus I have found it possible at high temperatures, above about 400° C., to realize moderate reaction as between nitrogen and hydrogen the resulting amide being a source of fixed nitrogen.

Flow through the discharge zone retards liberation of substantial amounts of potassium. In similar manner other fused compounds of two metals may be used to liberate the one which is slightly lower in decomposition potential. The negative ions or radicals need not necessarily be alike. It is so possible to separate two metals of nearly like decomposition potential whereas ordinary methods would release substantial quantities of each.

The treated melt, or product therefrom, may be passed into a zone of contact with a hydrocarbon and used to promote reaction thereof or there within. The melt may then be separated from reacted components as by decrease of temperature yielding separable crystals and the melt of lowered organic content recycled for treatment

in a zone of electrolysis. I intend to include means for carrying out this and other methods of the kind herein described. A byproduct of such reaction is frequently the hydroxide of the metal and it so becomes available for electrolysis as in admixture with chlorides. Organic and carbon-like products may be separated during or between treatments. Resinous products obtained from mineral oil treatment may be taken up as in a light solvent oil and used as a protective coating as for metals. Copal or other like substances may be mixed therewith and drying oils may be utilized in connection with such application. Used or formed caustic or metal may be reacted with vegetable, animal or fish oils and to dissociate the same and/or to make soap-like substances suitable for use in oils or other lubricants.

With sodium chloride, for example, the sodium and chlorine may be freed by electrolysis and the sodium used directly or in altered form such as that of sodamide for promotion of reaction while the chlorine may be used for treating benzol to form chlorbenzol which in turn may be reacted with ammonia to produce aniline which in turn is converted as by means of formaldehyde and cyanide into phenylglycine salt which may be reacted under the influence of the sodium or a derivative thereof such as sodamide formed by treatment with ammonia. Similarly toluol and other product may be chlorinated and with the addition of one or more chlorine atoms to each molecule.

The use of a mixture of benzol and toluol permits the use of inferior grades of coal tar distillate or distillate from petroleum which is of the general boiling range but which are of other than ordinary and simple ring form. Such products are preferably first treated with a metal with an unpaired electron such as sodium to remove condensable or rearrangeable substances. Thus mixtures containing toluol, benzol or the like may be treated with sodium with a resulting increase in concentration thereof and a corresponding decrease in concentration of substances which may react with sodium. Such reaction may be condensation or direct addition of sodium as to form a metallic salt. Oxidation may precede such treatment and under controlled potential so that noncyclic substances are removed therefrom or after condensation or neutralization as with sodium or a compound thereof.

Compounds with a double bond may be chlorinated quite easily and generally with material increase in the boiling point which is often greater than the increase in boiling point of benzol for example when it is chlorinated. Fraction may then be used to effect separation or concentration. Where two or more chlorine groups enter one or both may be replaced by a group such as ammonia or an organic radical as under the influence of free metal or derivatives thereof such as an amide or an alcoholate the selection depending on the peculiar properties of the particular oil being treated. Aldehydes may be used to yield association in a manner similar to those which have heretofore been used.

Chlorinated compounds may be hydrolyzed with water at high temperature preferably in the presence of alkaline products of reaction under the influence of the metal. The hydroxide and/or the sodium salts of organic compounds are often suitable as for facilitating the hydrolysis. The so-formed hydroxy-containing portion may be reacted to yield an addition prod-

uct such as an ester, an ether or other similar form such reaction being limited as desired.

In view of the complexity of reaction of distillate, particularly that derived from petroleum it becomes impossible to describe the exact mechanics of such reactions. The products formed seem in many instances to be much more complex than the indicated simple types of reaction which have been described. My process may be applied to the general type of reaction such as the one wherein chlorine and sodium are used and where the results obtained are of the general types which have been described. In such manner association may be brought about and the viscosity index and other properties are generally improved. Portions of low value may be coupled up or used as a quasi "mixture" in the formation of a preferred form which is of greater utility. Other halides may be so utilized.

In treating an oil with the free metal, the results obtained sometimes have a very high sulphuric acid absorption number. Thus for example one particular oil yielded fractions which varied from about 60 to 100. It is obvious that treatment by the usual sulphuric acid method, or its equivalent, would almost entirely dissipate such oil or render it unsuited for direct use. Such oils seem to be well adapted to the general steps of the treatment of which chlorination and subsequent replacement of the chlorine is an example. In such manner the preliminary treatment with sodium or its equivalent seem to remove from a few to about twenty percent of impurities which would if present interfere with subsequent treatment.

By carrying out a series of steps such as I have described as being used for preparation of indigo, it is possible to use the mixtures such as those obtained from petroleum and in which nitration or chlorination may have been used to introduce the amido group. The resulting dye-stuff is frequently of brighter or different and more desirable shade than ordinary indigo. The change may be towards the red or the green. When certain distillate is used the colors are dull but desirable being of the brown or dull purple or green type.

Previous methods of treating an organic compound in a manner equivalent to fusion have involved a time element which is variable as regards time. For example, in the manufacture of indigo, phenylglycine salt is added to solution of sodamide in a mixture of sodium and potassium hydroxide over a period of about an hour or two. Thus if a fourteen percent sodamide solution may be initially present and this amount is then reduced to about one or two percent as the salt is added, a portion of the salt is present for say two hours and initially in contact with fourteen percent agent. Later portions of salt contact only with say three or four percent of agent and for say but a half an hour or less.

My process preferably involves substantially more uniform contact as regards time and concentration for example as by being about the reaction within about half an hour and by means of a nearly uniformly active reagent held at say between about five and ten percent. This may be accomplished as by feeding the reagent into a zone to which the salt is also fed. In some such reactions the amount of melt such as caustic may be substantially reduced and instances practically or entirely eliminated. Thus as an example phenylglycine may be treated

directly with sodium or potassium in such manner as has already been described and preferably in an oil of petroleum or coal origin which may be in a form of a derivative. The selection being such as to give one or more desired properties such as solubility, viscosity, stability, boiling point and influence on the reaction such as have been previously described. Such a subject is preferably pretreated as with sodium, potassium or aluminum so that reactable materials are altered to a more stable form and/or removed.

The phenylglycine may be separated or purified by distillation under high vacuum, preferably within a couple of millimeters or so. The salt may be refluxed and/or distilled in association with a metal with an unpaired electron and purification or reaction thus promoted or influenced. An inert oily fluid may be used in such contact as a carrier or diluent to facilitate desired reaction. The indigo may be similarly treated and/or reduced and purified.

Molten metallic compounds of the general type described may be dehydrated by the passage of vapors of an oily substance therethrough or into contact therewith. Thus mixtures containing such metallic chlorides, hydroxides, silicates, phosphates, sulphates and other salts may be substantially reduced in aqueous content and gaseous or other fluids contained therein. As an example a mixture of sodium and potassium hydroxides may be passed through a tower in contact with vapors of xylol or naphtha or the like. The water content of say about one to ten percent may so be reduced to below about one percent and generally to a small fraction thereof. The carrier vapors may be recovered and recycled. Impurities of such carrier may be simultaneously altered or removed or this may be done by previous treatment in a manner already described. Such general procedure effects savings in cost and otherwise improve and facilitate operation.

Among metals which may be used or treated by methods herein described are beryllium, aluminum, magnesium, strontium, barium, lithium and aluminum and various inorganic salts, oxides and hydroxides thereof. Mixtures may be used. The objective of the treatment and the characteristics of the reacting or used components influence the selection of the metal or salt. In general optimum conditions can be obtained only by cut-and-try methods for each application.

The metallic agent used may be free or as a derivative and it may be in association with a hydroxide or a salt or an inert organic fluid. After contact with organic substances the melt may be treated by settling or centrifugal force and in general three layers will be established. The upper may be high in oily or other organic matter and the lower may be largely of particles such as crystals of separated compound. The control layer may be withdrawn and reused or treated before reuse. Such separation is preferably carried out at substantially constant temperature and with a temperature variation of less than about ten degrees centigrade. About an hour is generally required before withdrawals are started and in excess of about ten hours is required in some instances.

Details of usable apparatus are known or are described in prior applications. I do not limit my claims to the exact methods and means

as described. Other approximately equivalent methods and means may be used.

Features of my invention are illustrated in the drawings. Fig. 1 represents a vertical section through an electrolytic cell which may be used for carrying out my process although refinements and different design may yield more desirable results and perhaps be generally more satisfactory. In this schematic arrangement a container 1 is provided with an inlet 2 which may be used to deliver the material which is to be electrolyzed such as hydroxides, salts or oxides of inorganic metallic compounds of the general class as described. An outlet 3 may be provided with adjustment so as to provide an adjustable overflow the details of which general type are well known and easily provided.

The fused material or the equivalent may be passed into the cell as from a treating tower through which it may be recirculated and in the general manner as described in prior applications including Ser. Nos. 613,080 and 613,081 or this material may be obtained from recovery of production systems wherein aqueous or other solutions may be treated to concentrate and ultimately dehydrate the substance. The material is flowed and preferably at a speed considerably in excess of about ten feet per minute through zone 4 wherein electrolysis takes place. The metal such as sodium or another with one unpaired electron is released, say, at the electrode 5.

A suitable gauze 7 prepared similarly to a metal screen is placed as indicated and may be used in multiple. It may be used to retard diffusion or for connection to rectifying tube for return of electrons when non-conducting electrodes are used. Thus unidirectional current may be applied as described in other pending applications. This gauze is preferably hung from some suitable support which is represented as 8 and which is illustrated as being supported from cover plate 9 and supported therefrom. The screen or the like is preferably insulated from other parts and is so required when the electrical circuit demands segregation of the parts electrically.

An opening such as 10 may be provided in cover 9 for purposes such as inspection, cleaning and the like. The structure is preferably such that pressure other than atmospheric may be imposed on the melt, thus with a volatile substance within the cell a positive pressure may be desirable under some conditions as is also the case when reacting gases are involved and their reaction facilitated by such pressure.

Gases liberated at the surface of the electrode 6 may be collected in annular chamber 11 and vented through an outlet such as 12. If gases are liberated at electrode 5 they may be collected as in dome three and vented through an outlet such as 14. If this outlet is in multiple a gaseous or liquid fluid may be passed in and out in a manner to prevent accumulation therein of a mass of gas such as is often the cause of explosion in such apparatus. With liquid fluid it is obvious that appropriate elevations must be given to the various connections and to the liquid level. The cover or cover plate is preferably made removable.

An inlet for the introduction of gaseous or liquid fluid may be provided as represented by 16 with distributing header 17 with openings or outlets 18. This may be located in the lower portion of the cell as indicated or it may be placed in the upper part of the cell the exact location depending upon the fluids used and the purposes

thereof such as whether treatment is to be within zones 11, 13 or 4 or elsewhere.

The chamber 19 may be provided for a temperature control substance such as mercury. Vapors may be introduced through the pipe 20 and condensate drawn off through pipe 21. When cooling is required, connection to pipe 21 may be provided to maintain a liquid mass in chamber 19, the piping being such that the exothermic heat may be absorbed by causing the liquid in 19 to boil, the vapors passing to condensers connected to pipe 20. The latent heat of vaporous hydrocarbons which are to be treated by the melt or a component derived therefrom may be passed into heat transfer relation so as to control reaction. Thus liquid hydrocarbon may be volatilized in or close to the reaction or electrolysis zone.

One side of a source of a unidirectional or a direct current may be connected to pipe 22 which is connected to electrode 5 and insulated from the opposite side as by means of insulating material 23. The other side of the electric current may be connected to vessel 1 and thus to electrode 6. The current passes through the zone 4 acting upon substances such as fused alkali compound, mineral oil or chemical to be treated which may be passed therebetween. Deposited metal or migrated substance accumulating at or near the surface of the electrode 5 or 6 passes upwardly in and/or through the current of fused compound. Should decomposition or occurrence of substance exceed solubility it may rise more rapidly than the melt itself. Ammonia may be passed into 11 or 13 and used to react substances, thus sodium may for example be converted to sodamide. Nitrogen may be reacted with potassium or sodium or the like and this may be before or after hydride formation thereof. The nitrides thus formable in such matter may be protected by covering of inert fluid which may be liquid and oxygen may subsequently be added thereto. Other substances may be similarly treated in the same or equivalent general manner. Halogens as liberated when chlorides are treated may be passed into contact relation with organic matter in known manner and as for purposes as indicated. The discharged mass which may contain for example a 14% solution of sodamide or which may contain sufficient metal so that sodamide may be made therefrom and the mixture or solution adjusted to about such strength. Such mass may be used for general reaction. Thus phenylglycine may be fused to form the base for indigo.

The process may be carried out as illustrated in Fig. 2 or in prior applications. Suitable electrolytic effect may be carried out in cell 1. The fusing of the organic salt given as an example may be carried out in vessel 24 and gaseous ammonia vented through outlet 25 as the reaction progresses with agitation. The salt may be charged as by means of feed hopper 27, the finished fused mass being discharged through the outlet 28 into the dilution tank 29 and as either liquid or solid form. The tank 29 may have been filled with water by pipe 30. If air or ozone oxidation is used to precipitate indigo it may be introduced as by pipe 31 and bubbled through the mass.

The indigo may be withdrawn through 32 and concentrated and separated from dilute caustic as by countercurrent flow through thickeners 33 and 34 and filter 35. The fused mass may be treated prior to dilution so as to concentrate crystals of particles of the organic substance as regards the melt. Thus settling with very carefully controlled temperatures, preferably slowly fall-

ing, may be used. The portion withdrawn with less organic matter may be used for other fusion or passed through the cell or otherwise used. Thickened slurry from 33 is preferably mixed with water as in agitating chamber 37. The liquid from 34 may be used in 29. That from 33 may be concentrated as in evaporator 36 with steam connection 37' and vacuum connection 38. Concentrated caustic may pass from 39 to dehydrator 40 and be reduced to about .3% of water. Hydrocarbon vapors may be passed into contact with such melt in order to remove water or other substance which is volatile. Storage tank 41 may also be used to carry out dehydration by means of substance which may have been derived from the electrolytic process as indicated. The thus completely dehydrated melt may then be passed into the cell thus completing the cycle.

Ammonia gases liberated from the cell 1, the fusion pot 24 and the dehydrator 41 may be recovered as by passage through absorption towers 42 and 43 with water connections 44 and 45. Ammonia may be regenerated as in generator 46 with steam connection 47 and water connection 48. Evolved hydrogen or other gas may be vented as from 49 and utilized as for reaction or wasted. Cooling coil connections 50 are preferably provided. A near eutectic melt of two or more substances may be so used thus sodium and potassium hydroxides may be used for producing indigo.

I claim:

1. The process of producing an alkali metal which comprises passing a fused alkali metal chloride at controlled speed and under controlled potential through a well defined electrolytic zone so that successive quantities of the flow of chloride are subjected to a substantially constant current density for like time periods and at an appreciable rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a predetermined mixture of the metal and the chloride.

2. The process of producing an alkali metal by electrolysis and utilizing a byproduct of the electrolysis which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate appreciably in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride, quickly passing released chlorine into contact with a hydrocarbon and chlorinating said hydrocarbon and subsequently contacting a portion of the chlorinated hydrocarbon with alkali metal so freed to form alkali chloride.

3. The process of producing an alkali metal by electrolysis and utilizing the products of electrolysis which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride and passing released chlorine into contact with a hydrocarbon and chlorinating said hydrocarbon and passing a portion of the electrolyzed melt into contact with chlorinated hydrocarbon and so causing a reaction thereof.

4. The process of producing an alkali metal by electrolysis and utilizing the products of electrolysis which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride and passing released chlorine into contact with a hydrocarbon and chlorinating said hydrocarbon and passing a por-

tion of the electrolyzed melt into contact with chlorinated hydrocarbon and so causing a reaction thereof with the formation of metallic chloride.

5 5. The process of producing an alkali metal by electrolysis and utilizing the products of electrolysis which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride and passing released chlorine into contact with a hydrocarbon and chlorinating said hydrocarbon and passing a portion of the electrolyzed melt into contact with chlorinated hydrocarbon and so causing a reaction thereof and association of contacting portions of hydrocarbon.

20 6. The process of producing and utilizing an alkali metal which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride and recycling said mixture through a path including a region of vaporous hydrocarbons and said zone and so producing reaction within a portion of the hydrocarbon.

30 7. The process of producing an alkali metal and using the metal to promote a reaction which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride and recycling said mixture through a zone of contact with a hydrocarbon, causing reaction thereof and with inappreciable temperature change.

40 8. The process of producing and using an alkali metal which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride and reacting a gaseous fluid containing a hydrocarbon, which may be desirably altered by alkali metal, with metal of the mixture while flowing current through the chloride of the electrolytic zone.

50 9. The process of producing and utilizing an alkali metal while avoiding hazards inherent to use of the metal which comprises passing a fused alkali metal chloride through an electrolytic zone at a rate in excess of the rate of electrolysis and in a manner to deliver beyond the zone, a mixture of the metal and the chloride, excluding air from the metal during formation and thereafter while it is in existence and flowing the same into a contact zone and contacting a reactable hydrocarbon therewith and in dilution with an inert hydrocarbon at a temperature between the melting point of the chloride and about 400° C. and so promoting desirable reaction within the hydrocarbon.

65 10. In electrolyzing a fused mixture containing sodium and potassium hydroxides and forming free sodium and utilizing the same, the process which comprises flowing a fused mixture containing sodium and potassium hydroxides through a defined zone of electrolysis in amounts substantially greater than the amount of hydroxide decomposed by electrolysis and under a potential controlled so that sodium hydroxide is decomposed into free sodium at a rate substantially greater than potassium hydroxide is decom-

posed into free potassium and subsequently flowing the fused mixture so formed into a closely located contact zone whereat vapors of oil of petroleum containing an alterable impurity are treated at about the same temperature as electrolysis to alter the impurities with the consumption of appreciable amounts of sodium and removing the hydroxide mixture of lowered sodium content from the vapors and returning portions thereof to the zone of electrolysis for similar treatment therein.

15 11. In forming a mixture of a fused decomposable inorganic compound of an alkali metal and metal derived therefrom by electrolysis of a fused mass containing the compound and utilizing the metal and the compound for promoting desirable change in a hydrocarbon, the process which comprises flowing a mixture containing the fused decomposable compound through a defined zone of electrolysis in association with a second similar decomposable inorganic compound which requires a somewhat higher voltage to decompose the same and release free metal therefrom and at a rate appreciably greater than the rate of electrolysis, controlling the potential applied to the zone of electrolysis so as to release free metal from the first compound of lower decomposition potential while preventing substantial decomposition of the second compound of higher decomposition potential and applying freed metal and a portion of the second electrolyzed compound which has not been substantially decomposed into contact relation with a hydrocarbon to be treated and promoting desirable change thereof and wherein the masses of inorganic compound and metal derived therefrom are maintained molten and excluded from air throughout.

40 12. The process of producing alkali metal and chlorine and utilizing the same in situ, which comprises flowing a fused mass containing alkali chloride through a defined zone of electrolysis to yield free alkali metal and chlorine, quickly flowing the chlorine into contact with a hydrocarbon and chlorinating portions of the same in a zone of contact located near to the zone of electrolysis, contacting chlorinated hydrocarbon with free alkali metal which has recently been formed and so causing a desirable reaction of the hydrocarbon under the action of the metal and wherein the metal is maintained fluid and molten throughout its existence in the free state and with the exclusion of air throughout and application of the metal to the chlorinated hydrocarbon at a zone close to the zone of electrolysis.

55 13. The process of producing an alkali metal from an alkali metal chloride and utilizing the metal in admixture with the chloride while avoiding hazards and preventing loss of active metal, which comprises flowing a fused alkali metal chloride through a well defined zone of electrolysis at a rate which is appreciably in excess of the rate of electrolysis and in a manner to deliver beyond the zone a mixture of the metal and the chloride and quickly contacting the mixture with a hydrocarbon containing a component which may be desirably altered by contact with alkali metal and chloride and so promoting desirable alteration of a portion of the hydrocarbon and wherein the mass is maintained fluid and excluded from air throughout.

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