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ELECTROLYSIS OF ALKYL GRIGNARD-CONTAINING ELECTROLYTES

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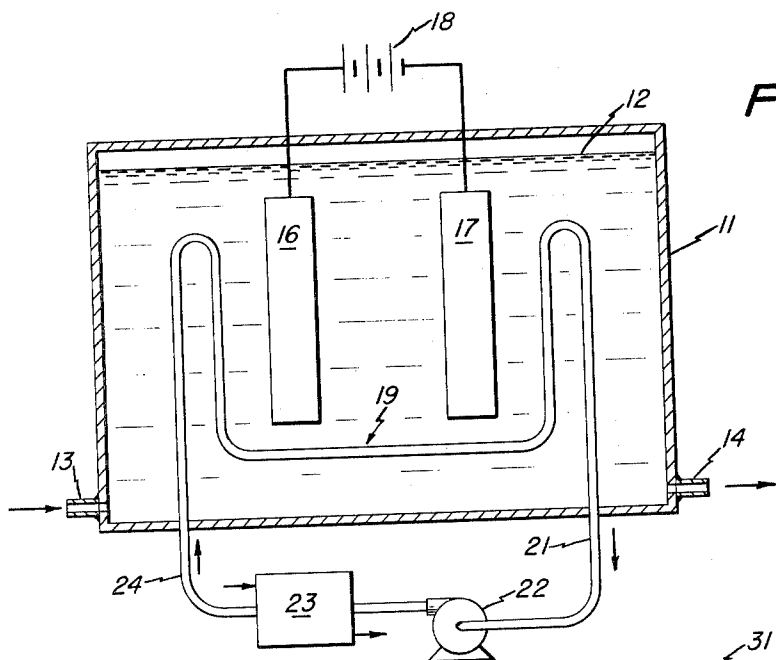


Fig. 1

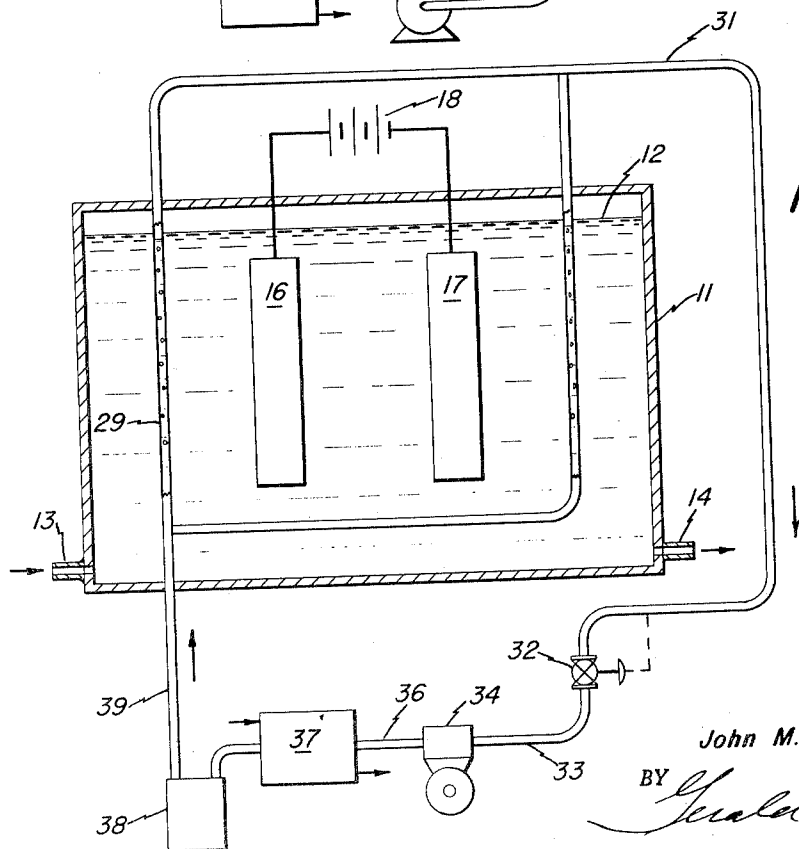


Fig. 2

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4 Claims. (Cl. 204—59)

This invention relates to electrolytic cells used in chemical conversion processes, and more particularly concerns a novel cooling system for such cells when employed in the electrolysis of alkyl Grignard-containing electrolytes.

It is heretofore known that organometallic compounds of such metals as zinc, aluminum, magnesium, cadmium, tin, lead, and others may be prepared by electrolyzing a Grignard reagent with an anode composed of the metal which is to form the organometallic compound. Such processes, by reason of their versatility, simplicity, and economy, are now becoming of increasing value. Nevertheless, certain construction and operating problems remain, and it is an object of the present invention to provide a unique solution to what has heretofore been the most troublesome of these.

When an electrolysis is being conducted, it is often desirable to maintain electrolyte temperature within a fairly close range. This becomes quite difficult in the electrolysis of alkyl Grignard electrolytes due to the comparatively high I^2R losses, coupled with unavoidable heat of reaction. It has heretofore been proposed to cool electrolytic cells by employing various coolants in coils or tubes disposed within the cell; however, the most convenient coolant, water, reacts violently with Grignard reagents to evolve heat and large amounts of hydrocarbon gas. Unfortunately, leakage of cooling water into the electrolyte is altogether too likely to occur in view of the thin cooling tubes and the corrosiveness of both water and the Grignard electrolyte. It is, therefore, a primary object of the present invention to provide a cooling system for such cells wherein any leakage between coolant and electrolyte will be substantially completely innocuous, and which, at all events, will not be hazardous to surrounding personnel.

Briefly, in accordance with the invention, an electrolytic cell employing an alkyl Grignard electrolyte and a consumable metal anode is cooled by indirect heat exchange with a coolant stream composed of the alkyl halide which corresponds to the alkyl Grignard electrolyte. That is, for example, if ethyl magnesium chloride is electrolyzed with a lead anode to produce tetraethyl lead, the electrolyte is cooled with circulating ethyl chloride. Thus, should there be any leakage, the coolant and electrolyte will be non-reactive.

In one aspect of the invention, the alkyl halide is maintained in the liquid phase, and is itself cooled by external heat exchange with an extraneous coolant such as water, which is not, however, permitted to come in the vicinity of the electrolyte. This embodiment has the advantage of economy of installation and simplicity of operation.

In another aspect, liquid alkyl halide is supplied to cooling coils disposed within the electrolyte, and is permitted to vaporize under controlled pressure. Thus heat produced during electrolysis is absorbed as latent heat of evaporation. The resultant alkyl halide vapors are then recompressed, cooled and condensed, and the resultant liquid is then available for return to the coils. It will be recognized that this embodiment is, in effect, a vapor compression type refrigeration system, and offers the advantages of large heat capacity for a relatively small coil size.

The invention will be more fully described and clearly

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understood in the ensuing description, which is to be read in conjunction with the attached drawings wherein:

FIGURE 1 schematically depicts an electrolytic cell cooled by recirculating liquid alkyl halide; and

FIGURE 2 schematically shows an elevation of a cell cooled by the vapor compression refrigeration system utilizing alkyl halide as refrigerant.

Before proceeding with a discussion of the respective figures, a few words may be said about the electrolytic process in general. Essentially, alkyl groups of from 1 to, say, 8 or more carbon atoms in an alkyl Grignard reagent, e.g. methyl magnesium chloride or ethyl magnesium chloride, are transferred by electrolysis to the "consumable" metal of the anode. As a result, the consumable anode metal, for example lead, is converted to the corresponding metal alkyl, e.g. tetramethyl or tetraethyl lead.

The alkyl Grignard electrolyte comprises the alkyl Grignard reagent together with an appropriate solvent. Known Grignard solvents require the presence of an ether or tertiary amine, such as diethyl ether, dimethyl ether of ethylene glycol, dibutyl ether of diethylene glycol, hexylethyl ether of diethylene glycol, triethylamine, etc. An additional ether, for example tetrahydrofuran, is often found to be of advantage for increasing electrolyte conductivity, as is the presence of a normally liquid aromatic hydrocarbon such as benzene, toluene, xylenes, etc. Lastly, the electrolyte may contain excess alkyl halide to react with magnesium metal plating out at the anode and thereby reconvert it to additional Grignard reagent. By way of example, a typical alkyl Grignard electrolyte prior to electrolysis may have an alkyl Grignard reagent concentration of about 1.5–3.5 Normal, an ether concentration of about 30–80 weight percent, about 10–40% tetrahydrofuran, about 20–50 weight percent benzene, and about 1–10 weight percent excess alkyl halide.

Conditions within a typical electrolytic cell depend largely upon cell design and considerations of thermodynamics and economics; consequently, they will vary widely depending upon the particular system. For the preparation of tetraethyl lead, a temperature within the range of about 20° C. to about 100° C., preferably about 20–50° C. and optimally about 25–35° C. is desired, while a current density at both anode and cathode within the range of about 0.2 to about 100 amperes per square foot of electrode area is disadvantageous. Relatively low voltages, of the order of about 20–30 volts, are usually preferred, although cell voltages of 50 volts and even higher may be utilized. Cell pressures may range from subatmospheric to low superatmospheric, say 60 p.s.i.g., and the electrolysis may be conducted batchwise, continuously, or semi-batchwise with intermittent or continuous addition of reactants. It is particularly noted that the inventive cooling system is suitable for any and all of the foregoing variations, which illustrates its exceptional versatility.

Turning now to FIGURE 1, an embodiment of the invention is depicted in simplified cross-sectional elevation. The cell proper comprises an outer jacket 11 containing electrolyte 12, which is admitted via conduit 13 and withdrawn via conduit 14. Anode 16, of lead or other consumable metal, is connected in circuit with cathode 17, of steel or other conductive material, and with a direct current power source 18. It will be appreciated that numerous arrangements of electrodes may be employed, including, without limitations, a plurality of flat plates, foraminous baskets containing lead shot, etc.

A coil or tube 19 is disposed in electrolyte 12 in direct heat exchange contact; that is, coolant within coil 19 can conduct heat from electrolyte 12 and thereby reduce or maintain the temperature during electrolysis.

Coil 19 may be finned, wound into a plurality of return bends, connected with similar coils or tubes in parallel or series-parallel arrangements, or otherwise constructed to afford a relatively high surface area.

Coolant in coil 19 is passed via line 21 and pump 22 through heat exchanger 23, where the alkyl halide coolant is itself cooled by indirect heat exchange with an external coolant, as for example water, and then passes via line 24 to coil 19.

A sufficient pressure is maintained on the alkyl halide coolant in coil 19 to maintain substantially all of the alkyl halide in the liquid phase. However, should the cell be run above capacity, it may be desirable to dispose a pre-cooler or condenser in line 21 upstream of pump 22 in order to avoid presenting any vapor to pump 22 and thereby avoid pumping difficulties.

It will be noted that any leakage in coil 19 would merely result in alkyl halide coolant flowing into electrolyte 12, or vice versa, depending upon the relative pressures in coil 19 and in the electrolysis zone. Should pressure in coil 19 exceed that of the electrolysis zone, alkyl halide would leak into electrolyte 12, and would merely increase the volume and pressure thereof, while not causing any serious chemical or thermal disruptions. Similarly, should electrolyte leak into coil 19, there will be no adverse reaction produced.

Turning now to FIGURE 2, the second or vapor compression refrigeration type embodiment is depicted. Identical elements in FIGURES 1 and 2 are designated with identical numbers. However, in this embodiment substantially all of the alkyl halide admitted to coil 29 is permitted to evaporate, and the resultant alkyl halide vapor is withdrawn via vapor line 31.

Tracing the flow of alkyl halide coolant in FIGURE 2, liquid alkyl halide, at a temperature equal to or below the boiling point at the particular pressure prevailing in coil or tube 29, is transported to coil 29 which is in heat exchange relationship with electrolyte 12. As the latter becomes heated during electrolysis, alkyl halide boils off. The resultant vapors pass through line 31 to back pressure control valve 32, which maintains a constant or controlled back pressure on line 31 and tube 29. Excess alkyl halide, over and above that necessary to maintain the constant back pressure, is conducted as a vapor via line 33 to compressor 34, which increases its pressure to that prevailing in tube 29. Compressed vapor leaving compressor 34 passes through line 36 and into heat exchanger 37, which functions as a condenser to condense the compressed vapor and provide a liquid recycle stream which collects in receiver 38 and is then sent to coil 29 via line 39.

Since the alkyl halide coolant or refrigerant in this FIGURE 2 embodiment is selected to correspond with the alkyl Grignard electrolyte 12 (e.g. methyl chloride for the electrolysis of methyl magnesium chloride), the pressure maintained by back pressure control valve 32 is selected to provide a desired constant temperature in coil 29, and thus a substantially constant temperature in electrolyte 12. Relationships between pressure and boiling point of the several alkyl halides may be found in the literature, and are given, for example, in Perry's "Chemical Engineers Handbook," second edition, section 23 (McGraw-Hill, 1941); "Physical Properties of Chemical Compounds, II," page 191 et seq., Advances in Chemistry Series (American Chemical Society, 1959); and Timmermans' "Physico-Chemical Constants of Pure Organic Compounds," page 210 et seq. (Elsevier, 1950). Thus, for example, with methyl chloride, a temperature of 25.0° C. is maintained in coil 29 by setting back pressure control valve 32 to maintain a pressure of 1199 millimeters mercury absolute on line 31.

The embodiment of FIGURE 2 is particularly advantageous in that it permits a relatively small tube or coil

29 to remove large quantities of heat from the electrolysis zone due to the relatively high heat of vaporization of alkyl halides. In addition, the vapor pressures of boiling alkyl halides at temperatures most highly desired for conducting electrolyses of alkyl Grignard electrolytes are generally fairly close to those prevailing in the electrolytic cell, and consequently even should there be any leakage in coil 12 only a small amount of alkyl halide or electrolyte will leak through.

Thus it is evident that an extremely useful improvement in electrolytic cell design has been provided according to the invention. By selecting as a coolant the alkyl halide corresponding to the alkyl Grignard electrolyte, any leakage between the two is rendered innocuous, and permits electrolysis to continue with no hazard to personnel in the area or to equipment. Furthermore, should a leak be detected, it is frequently possible to provide sufficient alkyl halide to the cooling coil so that the alkyl halide coolant will leak into the electrolyte in an amount corresponding to the normal utilization of alkyl halide in the electrolyte.

While the invention has been described in conjunction with specific embodiments thereof, it will be understood that these are exemplary only, and that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. For example, other alkyl halides may be used with corresponding other Grignard reagents, e.g. methyl bromide, ethyl iodide, n-propyl chloride, n-propyl bromide, n-butyl chloride, etc. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims.

I claim:

1. In an electrolytic process employing an alkyl Grignard electrolyte wherein heat is produced during electrolysis, the method of removing heat from the electrolysis zone which comprises passing a coolant stream of alkyl halide corresponding to the alkyl Grignard electrolyte in indirect heat exchange relationship with said electrolyte.
2. In an electrolytic process employing an alkyl Grignard electrolyte wherein heat is produced during electrolysis, the method of removing heat from the electrolysis zone which comprises passing a coolant stream of alkyl halide corresponding to the alkyl Grignard electrolyte in indirect heat exchange relationship with said electrolyte, withdrawing said stream, cooling said stream by indirect heat exchange with an external coolant, and recycling said stream.
3. In an electrolytic process employing an alkyl Grignard electrolyte wherein heat is produced during electrolysis, the method of removing heat from the electrolysis zone which comprises passing a liquid coolant stream of alkyl halide corresponding to the alkyl Grignard electrolyte in indirect heat exchange relationship with said electrolyte, permitting said stream to vaporize under controlled pressure, withdrawing the resultant alkyl halide vapors, compressing and cooling said vapors to condense the same, and recycling the resultant liquid.
4. In an electrolytic process for the preparation of tetraalkyl lead compound, wherein an alkyl Grignard electrolyte is electrolyzed with a lead anode, the method of removing heat from the electrolysis zone which comprises passing a coolant stream of alkyl halide corresponding to the alkyl Grignard electrolyte in indirect heat exchange relationship with said electrolyte.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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April 28, 1964

John M. Coppersmith

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 47, for "disadvantageous" read
-- advantageous --.

Signed and sealed this 18th day of August 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents