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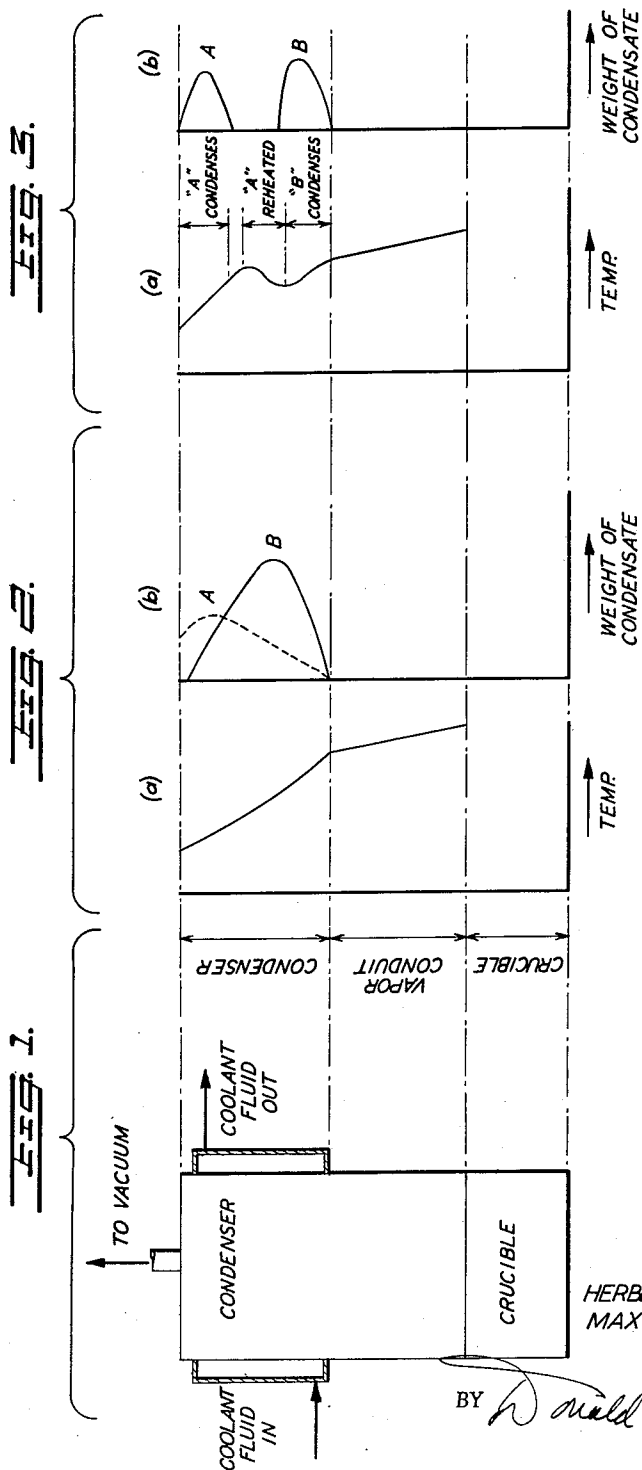
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3,136,627

PROCESS AND APPARATUS FOR SELECTIVE CONDENSATION OF METALS

Filed June 11, 1959

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

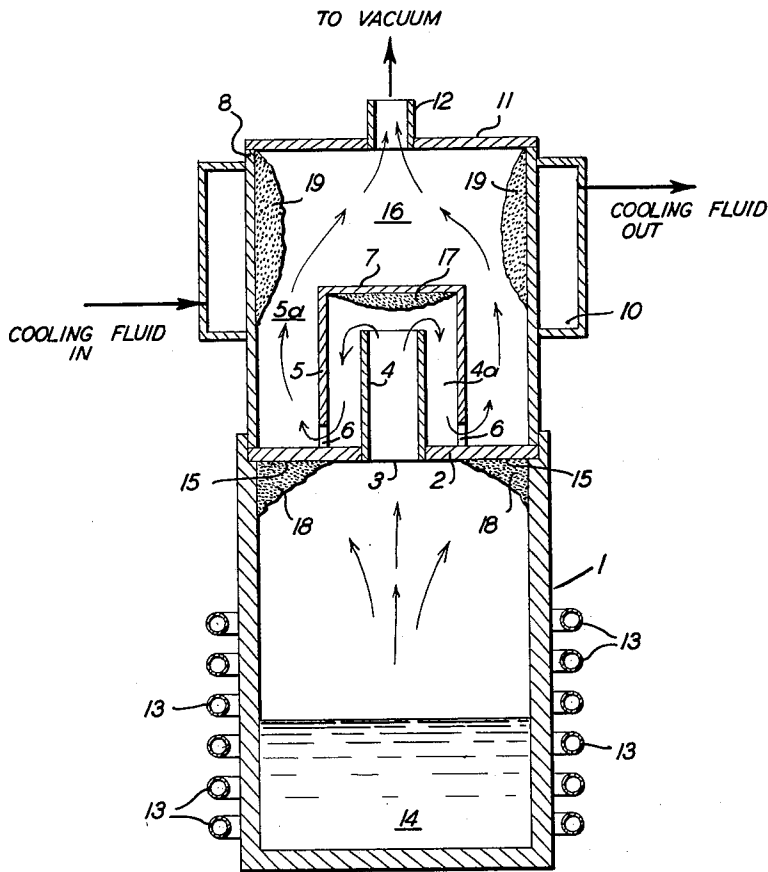


FIG. 4.

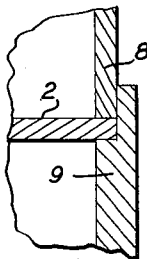


FIG. 5.

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1

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PROCESS AND APPARATUS FOR SELECTIVE
CONDENSATION OF METALS

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10 Claims. (Cl. 75-63)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention herein described and claimed may be
manufactured and used by or for the Government of
the United States of America for governmental purposes
without the payment of royalties therein or therefor.

This invention relates to the selective separation of
components from a mixture. More specifically, it relates
to the separation of components of such a mixture by
distillation and selective condensation of the constituent
compounds or elements in a high state of purity. In the
most specific form it pertains to the separation of in-
dividual metals in a high state of purity from a mixture
of metals or an alloy.

When distilling a charge of a military incendiary alloy,¹
at 600° C., assuming that the partial pressures obey
Raoult's law, the vapor can be shown to be initially near-
ly all cadmium with only a small percent magnesium
and a fraction of one percent of zinc, and no aluminum.
However, as the distillation progresses, the vapor com-
position changes so that it can be shown by calcula-
tion from the Rayleigh distillation equation that the
vapor contains equal proportions of magnesium and cad-
mium after about 10 percent of the alloy is evaporated
and that when the alloy is 30 percent evaporated the
vapor contains roughly about 75 percent Mg and 25
percent Cd. Cadmium is known to have a negative devi-
ation from Raoult's law, thus indicating that cadmium
cannot be separated from magnesium by simple dis-
tillation.

This was borne out in actual tests wherein a binary
alloy of 80 Mg-20 Cd was placed in a crucible having
a condenser connected thereto as shown in FIG. 1, de-
scribed below. Runs were made under vacuum at tem-
peratures of 550° C. and 700° C. and condensate was
removed from the wall of the condenser at intervals.
The following table gives the composition, and the per-
cent of evaporated charge.

Table 1.—Simple Distillation Tests on Prepared 80-20
Magnesium-Cadmium Alloys at 550° and 700° C.

Test No.	Temp., °C.	Percent of evaporated charge	Conden- sate, mg.	Percent Cd
A-1	700	5.9	80.0	20.0
A-2	700	15.9	80.4	19.6
A-3	700	26.5	80.1	19.9
A-4	700	36.5	79.6	20.4
A-5	700	47.6	81.5	18.5
B-1	550	4.1	70.3	29.7
B-2	550	11.8	77.3	22.7
B-3	550	28.2	77.2	22.8
B-4	550	38.8	77.1	22.9
B-5	550	45.3	83.6	16.4

These results indicate that separation by a fractional distillation
method is not feasible.

It is interesting to note that, if the partial pressures
followed Raoult's law, vapor having a composition of 80

¹ Average composition of incendiary alloy:

Elements:	Percent by wt.
Mg	75.4
Cd	19.1
Al	4.13
Zn	.45
Other	.74

2

Mg-20 Cd would have to come from an alloy containing
99 percent Mg and only 1 percent Cd. This indicates
that the composition of the surface is enriched in mag-
nesium because of the relative slowness with which
cadmium diffuses from the interior of the melt to re-
place that which has been evaporated. Cadmium, hav-
ing an atomic weight much greater than magnesium, will
not diffuse to the surface as rapidly as it is initially evap-
orated. Furthermore, as the surface is no longer en-
riched in cadmium the liquidus temperature rises so at
any temperature below the melting point of magnesium
the surface may be covered with a film of solid mag-
nesium-rich alloy, which also inhibits the evaporation of
cadmium.

Briefly, this invention consists of a method and ap-
paratus separating mixtures, which are difficult to separate
by fractional distillation because of nearly equal par-
tial vapor pressures, by selective condensation. The
apparatus consists of a retort having a lower crucible
portion and an upper cooled condenser portion. The
mixture is placed in the crucible, heated under reduced
pressure and the evolved vapors pass from the crucible to
the condenser along a tortuous path provided by a baffle
within the lower portion of the condenser.

Less volatile constituents condense near the entrance
to the baffle. The vapors impinge on a plate cooled to
condense some of the less volatile constituents admixed
with some of the more volatile components, and the un-
condensed vapors are reheated by heat exchange within
the baffle. After leaving the baffle the more volatile con-
stituents condense on the condenser walls.

It is an object of this invention to provide an improved
method and apparatus for separating the components of
a mixture of substances whose partial vapor pressures are
nearly equal to reasonable distillation temperatures, by
selective condensation under reduced pressure.

It is a further object of this invention to provide an
apparatus for separation by selective condensation, con-
sisting of a retort having a crucible and a connecting
condenser, wherein the mixed material is heated under
reduced pressure in the crucible and the evolved vapors
pass from the hot crucible region to the cool condenser,
and wherein baffle means are provided within the con-
denser for reversing the vapor path and causing a re-
heating of the vapors whereby a more clearcut separa-
tion of the various constituents in condensation is ob-
tained. Said baffle means provide tortuous path for the
vapors and act by virtue of the restrictive effect, to in-
crease the pressure in the crucible portion of the retort,
whereby the release of the vapors from the baffle passages
into the rest of the condenser area results in an expansion
and resultant cooling of said vapors.

The various figures in the drawing are as follows:

FIG. 1 shows, diagrammatically, a simple retort hav-
ing a lower crucible portion and an upper condenser
portion.

FIGS. 2 and 3 show a group of graphs wherein the
ordinate in each case is the distance along the distillation
zone of FIG. 2 and the abscissas are as indicated.

FIG. 4 shows a view in cross section of one embodi-
ment of the retort. FIG. 5 is a fragmentary view of a
portion of FIG. 1 without the condensed metal.

Without being bound to any theory, the failure of
separation by fractional distillation can be explained
as follows:

Consider a simple binary vapor composed of con-
stituents A and B whose partial vapor pressures are
nearly equal at the temperature and composition range
considered, A being the more volatile component. Al-
though there is a degree of selectivity in condensing the
constituents, the zones in which A and B condense over-
lap. The composition of the condensate at any point de-

3
pend on the temperature, the relative concentrations of the constituents in the vapor, and the relative rates of diffusion of the two species of vapor molecules. The separation is not sharp because as the B molecules they leave a preponderance of A molecules in the vicinity near the condenser wall. The large number of A molecules near the condenser wall increases the probability that some of them will condense prematurely with the B molecules. Under the circumstances, some of B molecules diffuse much farther than they would otherwise, and many of them condense belatedly with the A species.

This is illustrated in FIG. 2, portion (a) showing the temperature distribution along the length of the vapor path through the crucible and condenser of FIG. 1. FIGURE 2(b) shows the relative distribution of the constituents within the condenser. It is evident that constituent B is more abundant at the entrance zones of the condenser, while constituent A, being more volatile is condensed in greatest abundance at a more remote location in the condenser. However, the B condensate contains an appreciable amount of A and the A condensate contains an appreciable amount of B. In other words, the respective constituents are not selectively condensed so that they can be separated into two relatively pure fractions.

By increasing the temperature of the vapors at that location in their path after the bulk of element B has condensed, the separation of A from B may be enhanced. This is shown in FIG. 3 where the graphs show the effects of heating this vapor.

We have found the best mode of heating the vapor is to insert a baffle of suitable design in the retort, so as to reverse vapor flow for heat exchange relationship within the condenser. This is best shown in FIG. 4.

The apparatus, generally denoted as retort, consists of a crucible member 1 having mounted at the top in any suitable manner a plate 2 having a concentric opening 3 therein. A tube 4 mounted over the opening 3 extends vertically upward. Covering the tube 4 is a tubular cap 5 having apertures 6, at the bottom, and a cover 7 at the top.

Fastened to the upper part of the crucible by any suit-

4
Because the baffle reduces the diameter of the vapor path, the pressure buildup in the crucible 1 is greater than would normally exist without said baffle. Near the junction of plate 2 and crucible 1, there is a sharp drop in temperature due to the removal of heat by conduction through the outer wall. Condensation of at least some of the less volatile components occur at location 15 as solid deposits 18. The more volatile components remain in vapor state along with some of the less volatile constituents, and pass through tube 4. Only slight cooling occurs during the passage of the vapors through 4, and the heat that is lost is absorbed by the walls of tube 4. In the downward passage of the vapors between 4 and 5, most of the heat lost in transit is reabsorbed from the outer surface of tube 4. Some heat is lost from vapors condensing on cover 7, which is much cooler than the temperature of the impinging vapors because of its proximity to water cooling jacket 10. By proper spacing and control of heat exchange conditions, cover 7 may be maintained at a temperature below the condensing point of the less volatile constituents, and above the condensing point of the more volatile constituents. Solids 17 condense on cap 7 as shown. The more volatile constituents remain in the vapor state and pass downwardly through the relatively restricted annular space 4a between tube 4 and cap 5, during which the heat is absorbed from the walls of 4. The pressure and temperature of the more volatile constituent vapor is thus maintained above the condensation conditions until it emerges from the annular space 5a between cap 5 and sleeve 8. At this point there is a sudden expansion of relatively compressed vapors as they enter the large cool condenser space at 16. The resulting sharp drop in temperature causes the more volatile constituents to condense immediately on the walls of the condenser as deposit 19.

The operation of this invention is shown by the following specific example.

A military incendiary alloy of the composition given in the footnote was placed in crucible 1 and heated by electrical induction coil 13. Vacuum was applied through tube 12. The conditions and results of two runs are summarized in the following Table 2 as tests C and D.

Table 2.—Segregation of Constituents in Condensates Produced by Selective Condensation With a Vapor Baffle

Test No.	Temp., C.	Time, min.	System pressure, microns	Material	Chemical analysis, percent				Weight, gm.	Percent of total condensate
					Mg	Cd	Al	Zn		
C	500	300	50	Charge	75.4	19.1	4.3	0.45	5,588	
				Condensate 17	82.2	17.4	.01		581	18.2
				Condensate 19	0.1	98.4	.01	.87	473	14.8
				Condensate 18	98.8	.1	.01	Trace	2,134	66.9
D	550	300	50	Charge	75.4	19.1	4.3	.45	4,920	
				Condensate 17	63.4	35.8	.01		369	17.1
				Condensate 19	.3	99.4	.01	.30	308	14.3
				Condensate 18	99.9	Trace	Trace	Trace	1,478	68.6

able manner is a sleeve member 8. In the embodiment shown, see FIG. 5, this is done by means of a shoulder at the upper end of crucible 1. Plate 2 and sleeve 8 fit into the shoulder 9 in the manner shown, and the structure can therefore be readily disassembled. Sleeve 8 is cooled by a heat exchanger 10, attached around the outside of the sleeve to cover substantially all the outer surface of the sleeve between its upper edge and that circumferential part of the sleeve in close proximity to the cover 7 of the cap. The upper part of the sleeve is covered by a plate 11. Tube 12 passing through plate 11 is connected to a vacuum pump. All joints shown are close fitting and/or gasketed to prevent leakage.

In operation, the vapor passes through tube 4 and is cooled slightly. Heat is absorbed by the walls of 4 and is transferred to the vapor passing outside of the tube, which produces the retrograde temperature distribution shown in FIG. 3.

As shown in the table, condensates 18 and 19 are relatively pure metal. Condensate 17 is a mixture of cadmium and magnesium which can be recycled in the process.

Analogous results are obtained by employing a zinc-cadmium and a zinc-magnesium alloy in the above method.

It is not necessary that in the case of metal mixtures that the components be alloyed together. Under certain circumstances it is feasible to separate particulate mixtures of metals in this manner. While in the example the alloy was heated to melting temperature, this is not essential. The process may be operated where feasible under sublimation conditions, where the vapor pressures are high enough to cause evaporation at a relatively rapid rate. Materials other than metals may be separated in this manner, such as mixtures of organic compounds or inorganic salts.

The materials of construction employed in the retort are governed by properties of the substances treated. In

the case of the alloy shown, carbon lined mild steel is suitable. With organic or inorganic compounds, glass may be necessary.

It is obvious various other arrangements and substitutions may be made in the method and apparatus without changing the essential inventive concept. Thus, instead of having the cooling means surrounding the upper zone of the condensing sleeve, a cooling well may be mounted in said zone. Any of the common means known to the art may be employed for joining the various sections of the retort.

We claim:

1. A method for separating a mixture of metals having different melting points and volatilities by vacuum distillation and selective condensation which comprises; placing the mixture into an evaporation zone, heating the mixture to a temperature at which at least some of the metals have vapor pressures sufficient to cause evaporation at a relatively rapid rate, passing the evolved vapors to a condensation zone, said vapor tracing a path having an initial, intermediate and final section, each of said sections having an entrance and a rearward portion, said evaporating and condensation zones being under a reduced pressure, cooling the entrance of the initial section sufficiently to condense at least one of the less volatile metals, passing the vapors through the initial section of the vapor path with only slight cooling, impinging said vapors at the exit of said initial zone onto a surface cooled to just below the condensing point of said less volatile metal, passing the uncondensed vapors through the intermediate section, increasing the temperature gradient along the vapor path of the intermediate section sufficiently for heating the vapors to prevent the condensation of the more volatile metals, passing the vapors through the final path section, and decreasing the temperature gradient along the vapor path of said final section for cooling the vapors whereby at least one of the more volatile substances is condensed.

2. A method for separating a mixture of metals having different melting points and volatilities by vacuum distillation and selective condensation, which comprises; placing the mixture into an evaporation zone, heating the mixture to a temperature at which at least some of the metals have vapor pressures sufficient to cause evaporation at a relatively rapid rate, passing the evolved vapors upwardly from said evaporation zone, cooling the vapors sufficiently to condense at least one of the less volatile metals, passing the remaining vapors through a first restricted, elongated zone, impinging said vapors at the end of said restricted zone onto a surface cooled to just below the condensing point of said less volatile metal, whereby an additional less volatile metal condenses thereupon, passing said vapors downwardly through a first annular space surrounding said elongated zone and in heat exchange relationship therewith, whereby the vapors in the first annular space are heated, passing the vapors from said first annular space upwardly into a second annular space surrounding the first annular space and communicating therewith, cooling and expanding the vapors from said second annular space into a relatively cooler condensation zone, whereby cooling, and condensation of at least one of the more volatile metals takes place.

3. A method for separating magnesium and cadmium from mixtures consisting essentially of these two metals by selective condensation which comprises; placing said mixture into an evaporating zone, heating said mixture to a temperature at which melting takes place and at which the magnesium and cadmium have vapor pressures sufficient to cause evaporation at a relatively rapid rate, passing the evolved vapors to a condensation zone, said vapors tracing a path having an initial, intermediate and final section through said condensation zone, said evaporating and condensing zones being under reduced pressure, each of said sections having an entrance and rearward portion, cooling the entrance of the initial section sufficiently to condense at least some magnesium, said condensed mag-

nesium being relatively pure, passing the vapor with only slight cooling through the initial section, impinging the vapors on a surface cooled just below the condensing point of magnesium, whereby additional magnesium present in the vapors is condensed, together with some cadmium, increasing the temperature gradient along the vapor path of said intermediate section sufficiently for heating the vapors to prevent condensation of cadmium, passing the uncondensed vapors through the intermediate section, passing the metal vapors consisting essentially of cadmium into the final section, and cooling the final section sufficiently to condense said cadmium vapors at the rearward portion thereof.

4. The method of claim 2, where the mixture is an alloy consisting essentially of a magnesium and cadmium.

5. The method of claim 2, wherein the mixture is a binary alloy of magnesium and zinc.

6. The method of claim 2, wherein the mixture is a binary alloy of zinc and cadmium.

7. The method of claim 4, wherein the mixture is an alloy having the composition Mg, 75.4%, Cd, 19.1%, Al, 4.31%, Zn, .45%, other .74%.

8. A method of separating magnesium from cadmium in an alloy containing Mg, 75.4%; Cd, 19.1%; Al, 4.31%; Zn, .45%, which comprises placing said alloy in an evaporation zone, heating said alloy to a temperature of about 550° C. under a pressure of about 50 microns of mercury, passing the evolved vapors upwardly from said evaporation zone, cooling the vapors sufficiently to condense a portion of the magnesium in relatively pure form, passing the remaining vapors through a first restricted elongated zone, impinging said vapors at the end of said restricted zone onto a surface cooled to just below the condensing point of magnesium, whereby additional magnesium together with some cadmium condenses, passing the remaining vapors through a first annular space surrounding said elongated zone and in heat exchange relationship therewith, whereby the vapors in the first annular space are heated, passing the vapors from said first annular space upwardly into a second annular space surrounding the first annular space and communicating therewith, expanding and cooling the vapors from said second annular space into a relatively cooler condensation zone, whereby cooling and condensation of cadmium takes place.

9. An apparatus for separating the components of a mixture by selective condensation which comprises, an evaporator, a condenser in communication with said evaporator, said condenser, having an upper and lower portion and an inner wall providing a condensing surface for the most volatile of the components to be separated, apertured separating means dividing said evaporator from said condenser, a condensing surface for the least volatile of said components being provided by that part of the separating means inside the evaporator, baffle means within said condenser, said baffle means comprising a first inner conduit member generally parallel to the condenser and connected to said separating means, said conduit member communicating with the evaporator via said aperture, a cap member having side wall means surrounding said first conduit member and spaced therefrom to define a first annular space, said cap member being spaced from the condenser's inner surface to define a second annular space, the cap member having a closed top portion and apertured at the lower portion of the side wall means, said top portion providing on its internal side an additional condensing surface, said cap member extending up into the lower portion of the condenser, and cooling means adapted to cool the upper portion of the condenser.

10. An apparatus for separating the components of a mixture by selective condensation which comprises, an evaporator, a tubular condenser in communication with said evaporator, said condenser having an upper and lower portion and an inner surface, apertured separating means dividing said evaporator from said condenser, a first condensing surface for one of the components to be

separated being provided by that part of the separating means inside the evaporator, baffle means within said condenser, said baffle means comprising a first tubular member having its axis along the axis of the condenser, said tubular member communicating with the evaporator via 5 said aperture, a second tubular member having upper and lower ends surrounding said first tubular member and concentric therewith, said second member being longer and greater in diameter than said first member, and extending into the lower portion of the condenser, cap means closing 10 the upper end of said second member, said cap means providing on its internal side a second condensing surface, the space between said tubular members being designated a first annular space, said second tubular member being 15 spaced from the inner surface of the condenser and defining therewith a second annular space, said second tubular member having apertures at the lower end to form a communicating passageway between the first and

second annular spaces, and a cooling means surrounding the upper portion of the condenser whereby the said inner surface of the condenser provides a third condensing surface for another of the components to be separated from the mixture.

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