May 15, 1962 K. C. D. HICKMAN 3,034,700

METHOD OF PRODUCING HIGH VACUUM

Filed March 11, 1960 2 Sheets-Sheet 1

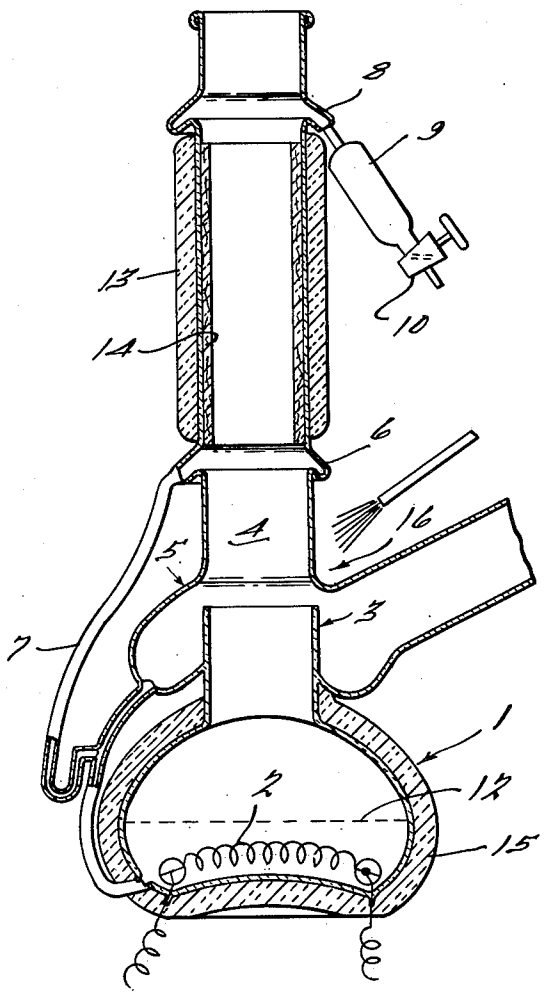

FIG. 1.

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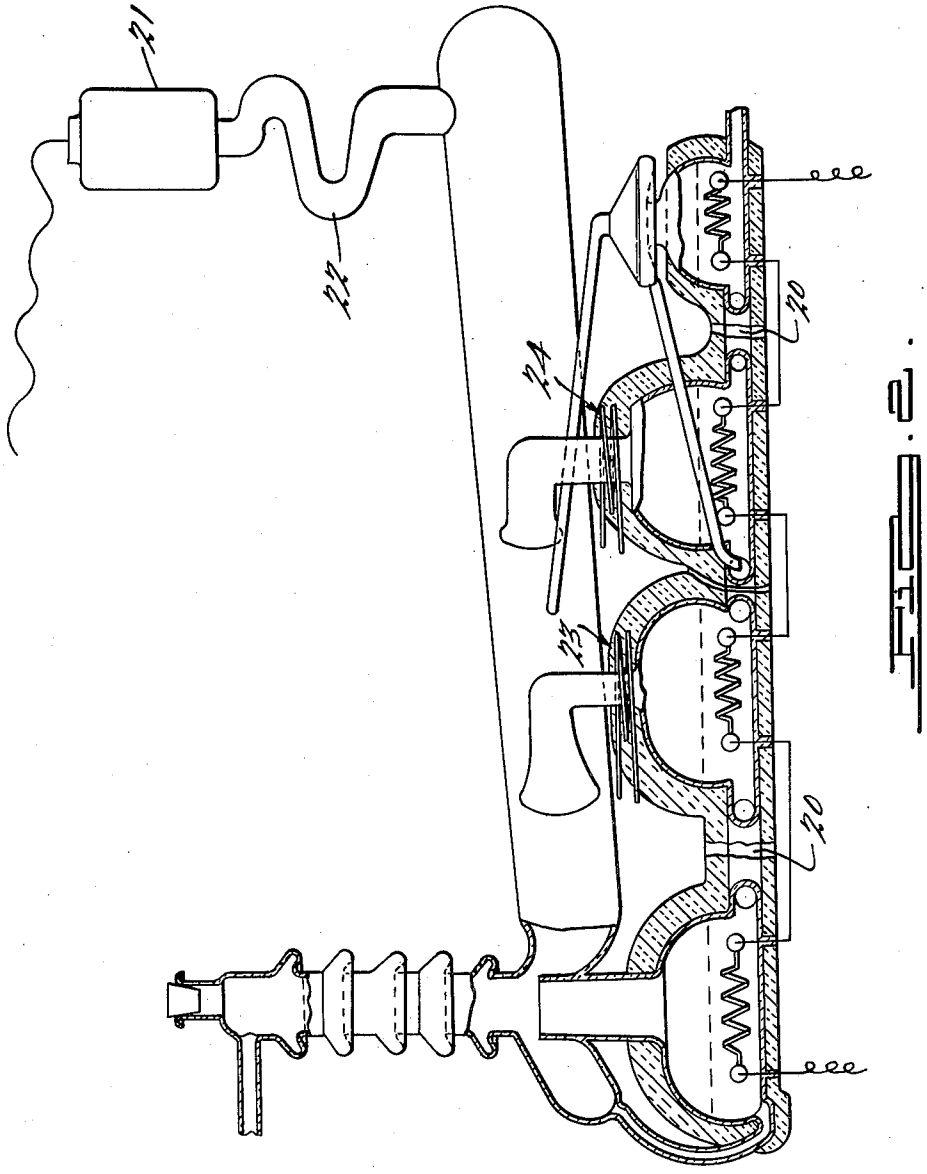

Fig. 2.

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METHOD OF PRODUCING HIGH VACUUM

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4 Claims. (Cl. 230—101)

This invention pertains to improvements in materials and apparatus for the production of high vacuums, and is concerned particularly with working fluids for use in vapor-actuated pumps variously known as diffusion pumps, condensation pumps, and vapor booster pumps.

The original Gaede-Langmuir condensation pump employed mercury as a working fluid, and mercury remains in use today. Wider use, however, has been made of high boiling organic fluids introduced by Burch in 1927. U.S. Patents #1,857,506, #1,857,508, #2,147,488, and #2,147,479 describe groups of individual organic compounds, liquid at room temperature, which have special advantages as working fluids in vapor pumps and can produce very high vacuums without use of a specially cooled trap. Two of these fluids, 2-ethyl hexyl phthalate and 2-ethylhexyl sebacate, available as "octoil" and "octoil S," have been in wide use for many years and are accepted as standards of performance. "Vacuum Pumps and Pump Oils," articles by applicant here, appearing in the Journal of The Franklin Institute, vol. 221, Nos. 2 and 3, February and March, 1936, discuss the operation of such working fluids in the production of high vacuums. Other compounds, particularly certain silicone oils, equal the foregoing in ability to produce high vacuum and exceed them in thermal stability.

In the last few years, notably since the advent of high energy particle accelerators and other nuclear and atomic devices, still higher vacuums have become necessary and the vacuums produced by existing fluids, even when used with auxiliary refrigerated traps, have left much to be desired so that, in some cases, they have been discarded in favor of so-called ion and "getter" pumps which vaporize titanium and other reactive metals. Satisfactory though these new pumps are from the point of view of end use, they are expensive and relatively difficult to operate. There is thus an acute need for liquid pump fluids useful in vapor-actuated pumps to attain a completely new order of high vacuum performance, with or without cooled traps.

An object of this invention is to supply organic pumping fluids capable of producing vacuums which, without a cooled trap, are 10–100 times better than have been obtainable with previous fluids under the same operating conditions.

Another object of the invention is to provide fluids which can be heated to and used at higher boiler pressures and/or higher temperatures than hitherto known in the art, so that greater thermodynamic efficiency may be secured and pumps can be constructed which operate against unusually high fore pressures.

Other and further objects of the invention will be apparent from the following description and claims which set forth the best mode contemplated of carrying out the invention. Other embodiments of the invention may be used without departing from the scope of the present invention as set forth in the appended claims.

In the drawings, of which there are two sheets:

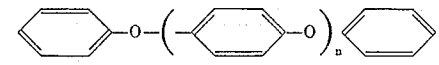
FIG. 1 is a vertical sectional view of a single stage vertical glass vapor-actuated pump in which the working fluids herein disclosed and claimed may be used for the production of high vacuums; and

FIG. 2 is a vertical sectional view of a three-stage fractionating pump in which such working fluids may be used for the production of high vacuums.

The pumping fluids which I have discovered belong to the class of the polyphenyl ethers and the polyphenoxy benzenes, and for convenience they are referred to herein as polyphenyl ethers. The materials are usually named either as benzene derivatives or as ethers, according as to whether they have odd or even numbers of benzene rings, and have the typical construction:

(1)

(2)



Such materials may be prepared according to any of the known methods or obtained from various commercial sources.

The first type of polyphenyl is the meta-, and the second para- linked. For the highest vacuums, the metas are generally to be preferred because of their exceptional thermal and oxidative stability at high temperatures. Mixtures of meta- and para- come next, although para- and ortho- types and internal and physical mixtures of meta-, and ortho- are useful and are within the scope of this invention. Advantages of mixed isomers are lowered melting points and commercial availability. Mixtures of the compounds themselves but of molecular weight other than the isomeric forms are also contemplated. Thus a useful working fluid would be a 4-ring phenyl ether or mixture thereof, plus a 5-ring phenyl ether or mixture thereof in a fractionating pump. The 4-ring compounds would gather at the fore pressure and the 5-ring compounds at the fine pressure end of the pump. The invention contemplates a single vapor-actuated pump or a train of such pumps in which one or more of such ring compounds from 3 to 7 are employed.

The 3-ring ethers with $N=1$ in Equation #1 provide excellent fillings for those booster pumps which are designed to operate against backing pressures of .2–20 millimeters to produce intermediate vacuums in the range of 1 millimeter to 1 micron.

Their high melting points, 141° C. for the meta- compound, 203° C. for the ortho-, and 171° C. for the para-, make it desirable to use mixtures of two or all three isomers to avoid solidification in parts of the pump.

The 4-ring compounds, either singly or as a mixture of isomers, exert a true vapor pressure of less than 10^{-6} mm. at elevated room temperature (100° F.) and provide highly robust fluids to create vacuums comparable to those obtainable with previous pump fluids. I have found particularly useful the 5-ring meta-ether of the general formula $C_{30}H_{22}O_4$ which exerts a true vapor pressure of less than 10^{-12} mm. Hg at summer room temperature. Very many isomers are possible and a synthesized mixture may be a mixture of such isomers which remain liquid when the individually pure compounds might be solid. I include, however, within my invention all polyphenyl ethers and phenoxy benzenes in the range of 3 to 7 phenyl groups linked by 2 to 6 oxygen atoms and of molecular weights between 264 and 641 and mixtures thereof which remain liquid under the operating conditions of a vapor vacuum pump. Particularly useful are mixtures which remain permanently fluid at room temperature.

These polyphenyl ether compounds and their mixtures have surprising characteristics as condensation pump fluids vis-a-vis conventional working fluids. They have lower vapor pressures and higher boiling points than pump fluids heretofore employed, and a very much higher resistance to thermal decomposition and oxidization. A comparison of these properties of the poly-

phenyl ethers and prior art working fluids is shown in Table #1, as follows:

TABLE #1

	Decomposition Temperature [a] ° C.	Resistance to Oxidation	Boiling Point 1 mm. Hg ° C.	Extrapolated Vapor Pressure 25° C./mm. Hg	Lowest diffusion 1-stage, mm. Hg	Lowest Measured Blank-off Pressure in Glass Pump 3-stage Fractionating, mm. Hg
2-ethyl hexyl sebacate	272	good	[b] 218	[b] 2×10^{-9}	5×10^{-6}	7×10^{-8}.
Silicone 704	394	excellent	[c] 250	[c] 1.7×10^{-8}	[c] 4×10^{-6}	1×10^{-8}.
Hydrocarbon pump oil	338	poor		[c] 5×10^{-8}	[c] 1.9×10^{-5}	5×10^{-7}.
Phenyl Ethers:						
3-ring	400	excellent	[a] 155-175	1×10^{-5}—1×10^{-6}	1×10^{-5}—1×10^{-6}	
4-ring	433	do	[a] 210-250	5×10^{-8}—7×10^{-9}	1×10^{-6}	2×10^{-8}.
5-ring	460	do	[a] 260-300	$<1\times10^{-12}$	5×10^{-8}	5×10^{-10}.
6-ring	460	do	[a] 320-365	$<1\times10^{-15}$	5×10^{-8}	1×10^{-9}.
7-ring	450	do	360-400	$<1\times10^{-13}$	1×10^{-7}	

[a] Monsanto data "Preliminary Report on the Polyphenyl Ethers," Bulletin No. A.V. 5, May 1959.
[b] Vapor Pressure of Phlegmatic Liquids, II. High Molecular Weight Esters and Silicone Oils. E. S. Perry and W. N. Weber. Journal American Chemical Society 71 3726 (1949).
[c] A New Silicone Diffusion Pump Fluid: A. R. Huntress, A. L. Smith, B. D. Power and N. T. M. Dennis, Symposium on on Vacuum Technology, 1958, p. 104-111. Pergamon Press, New York.

The polyphenyl ethers are often prepared by interlinking halogen derivatives with elimination of halogen, and an essential step in purification of the finished ether so prepared is removal of the last trace of halogen. This may be accomplished in any of the well-known ways, such as treatment with sodium exthoxide in ethanol with subsequent washing in water and drying. Another required step in purification is to remove light ends and thermally labile or oxidizable material, which can be done by prolonged moderate heating under vacuum or bubbling an inert gas or dry air at temperatures below 200° C. through the ethers, preferably under vacuum. For highly critical use I subject the material, after preliminary chemical and physical clean-up, to a slow distillation under high vacuum, rejecting the first 1% to 5%, or even 25%, and the last 1% to 5% of the distillate. By way of example, only the 5-ring compound is obtained as a mixture of isomers in the fraction distilling between 210° and 230° C. at $\frac{1}{10}$ mm. absolute. The rejected fractions are also superior pump fluids, judged by previous standards, and may be employed for less critical use, for instance in a fore or booster pump. Part of the purification procedure may include treatment with an absorption grade alumina or activated charcoal or dessicated silica gel, either before or after distillation.

Where the manufacturer of polyphenyl ethers has prepared a particularly pure batch of such ethers, I may omit one or more steps in the purification procedure—such, for instance, as the chemical pretreatment or the highly critical vacuum distillation. Also in those pumps that are fitted with means for rejecting fore vacuum distillate, I may increase the quantity of the primary charge and reduce the volume to normal by distilling a substantial fraction directly out of the pump. Whether, therefore, the polyphenyl ether fluids are conditioned for high vacuum use during manufacture or separately thereafter or in the pump itself, I regard the operating fluid so produced as coming within the scope of my invention.

By fractional distillation a specific polyphenyl ether can be obtained with a purity exceeding 80%, with the balance isomers and/or inert compounds. For most applications a mixture of the isomers of a 3, 4, 5, 6 or 7-ring polyphenyl compound will be satisfactory, but such mixtures need not be limited to the isomers of any specific ring compound; that is, a mixture of two or more of the ring compounds within the group indicated will be satisfactory.

Because the fluids boil at such high temperatures, it is feasible to use simple air cooling of the pump diffuser and to keep certain parts of the pump hotter than usual. This greater variation in temperature throughout the pump has the doubly advantageous effect of rejecting any self-generated impurities and also impurities acquired externally, such for instance as volatile substances coming from the evacuated chamber, or dirt and grease solvents, etc., remaining in the pump from a poor attempt at cleaning.

To produce high vacuum in accordance with my invention, I place a polyphenyl ether or mixture as herein disclosed in any suitable vapor-actuated pump, such as a single stage glass vertical pump, a three stage glass fractionating pump, or a "Langmuir inverted" type of metal pump, either single compartment or fractionating.

Where a polyphenyl working fluid embodying the invention is merely substituted for the old in a conventional pump, the heat requirements of the polyphenyl ethers may be as much as 25% to 50% greater than required for conventional working fluids, such as Octoil. However, I have found that by modifying the pump so as to cool the diffuser behind the jet to catch backstreaming molecules, but drastically cutting the cooling in front of the jet, I can maintain a long column of forwardly moving pump fluid vapor, and the longer this column the less chance the molecules have of diffusing backstream. The chimney of the inverted type Langmuir pump can be lengthened so that a long hot diffuser region can be accommodated below the jet, thereby diminishing greatly the heat requirements. This expedient improves the ultimate vacuum and at the same time conserves so much heat that a pump thus modified may require no more, or even less, heat than an unmodified pump would using conventional working fluids.

Because of the high thermal stability, it is practical in the case of a single stage vertical glass pump or any combination of stages to surround the upper or exit portion of the diffuser or receiving jet with heavy thermal lagging. In the case of an upwardly directed jet, means for catching rejected distillate and impurities are provided at the top of the pump, and I may employ any retention means, such for instance as a glass fibre fabric, for lining the inside of the diffuser walls to provide both thermal lagging and liquid hold-up. Such a pump is illustrated in FIGURE 1, where a glass boiler **1** is provided with heater element **2** formed of a resistance wire, in the well-known manner. A jet **3** cooperates with diffuser **4** fastened to the usual glass manifold **5** connected with the closed system to be evacuated. A shallow alembic **6** is connected with manifold **5** and boiler **1** by branched tube **7**. A second alembic **8**, a side tube **9**, and a closure **10** complete the structural part of the pump. A filling of polyphenyl ethers is placed in the boiler **1** to a depth shown at **12** permitting sufficient reserve so that the alembics and side tubes may be filled with liquid without the heater becoming bare. Lagging **13**, conveniently formed by a pad of glass wool batting, is applied around the upper portion of the diffuser and optionally a glass fibre fabric sleeve **14** is placed in the diffuser. The pump boiler may be lagged as at **15**, and a

small air blast is conveniently directed at the region **16** while the pump is in operation.

Example 1

Using the pump of FIGURE 1, charged with a purified amount of the 5-ring meta polyphenyl ether and attached to an ionization gauge of the type known as VG–1–A, a reading indicating a vacuum of 5×10^{-8} millimeters was obtained on blank-off at an ambient temperature of 80° F.

Example 2

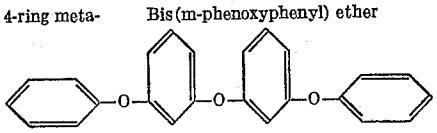
150 grams of a purified sample of the 5-ring polyphenyl ether isomers were placed in a 3-stage glass fractionating pump of the type shown in FIGURE 2, except that the connecting tubes between the boilers were lengthened and provided with means such as loops **20** to prevent back diffusion of the pump fluids during their forward travel. A Bayard-Alpert gauge **21**, selected because of its ability to make the lowest known pressure measurements, was sealed by a wide bore bent glass tube **22** to the closed low pressure end of the pump. The pump was heavily insulated with glass wool batting to conserve heat, and auxiliary heating coils **23** and **24** were placed around the necks of the middle and high vacuum jets further to minimize loss of heat. The glass pump was evacuated by an oil sealed mechanical fore pump and heated by an electric current at 95 volts delivering 225 watts.

After one hour the fore pressure measured 11 microns by hot wire gauge and the fine pressure 5×10^{-8} mm. Hg by the Bayard-Alpert gauge. The pressure fell successively to 1.4×10^{-8} in the next hour and to 1.7×10^{-9} in four hours. Next day a pressure of 6×10^{-10} mm. was recorded and maintained continuously. The temperature of the low pressure end of the glass pump was 100° F. and the ambient temperature of the laboratory at the test bench was 80° F. No trapping or refrigeration of any kind was used other than the bent glass tube **22** which remained slightly above ambient temperature. The low pressure end of the pump was then torched with a gas flame until its temperature was 200° F.±5°. The Bayard-Alpert gauge registered a rise of pressure to 5×10^{-9} mm. which shortly relapsed to 5×10^{-10}, with pump manifold at 100° F.

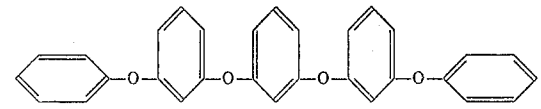
In a re-test, air was admitted to the pump to atmospheric pressure for 5 minutes while the pump was hot (but with the heating current off), after which fore vacuum and heating were again restored. Gauge readings fell to 3×10^{-8} mm. in 35 minutes, 5×10^{-9} in 75 minutes, and 1×10^{-9} in two hours. Later a limiting reading of 5×10^{-10} was recorded. These pressures are 100 times lower than have ever been recorded in a condensation pump under similar circumstances, and there is reason to believe that the actual pressures obtained were lower, since the Bayard-Alpert gauge, like other ionization gauges, is beset by secondary effects such as X-rays at these very low pressures.

Other specific examples of working fluids embodying the invention are:

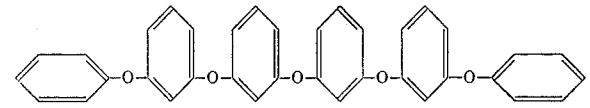
4-ring meta- Bis(m-phenoxyphenyl) ether



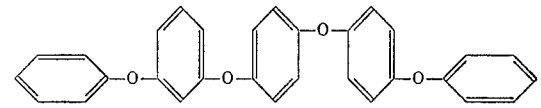
5-ring meta- m-Bis(m-phenoxyphenoxy)-benzene



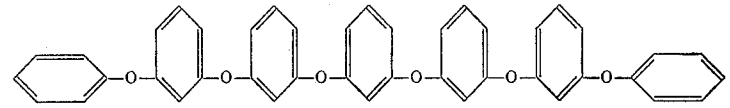
6-ring meta- Bis[m-(m-phenoxyphenoxy)-phenyl] ether



5-ring meta-para



7-ring meta- m-Bis[m-(-phenoxyphenoxy)-phenoxy] benzene



When the high boiling polyphenyl ethers are contaminated with organic liquids of greatly inferior thermal stability or are used in admixture with pump oils of much lower stability, the impurities or admixed oils become decomposed with liberation of gas which spoils the vacuum. In a similar manner, metals which contain zinc, lead or tin, metallic salts and halogenated solvents all can cause decomposition if exposed to the polyphenyl ethers at their normal temperatures of operation in the pump. Failure to reach the vacuum described according to this invention can be due to any of the forms of contamination above mentioned.

While I have described preferred embodiments of my invention, it is understood that these are capable of modification, and I therefore do not wish to be limited to the precise details set forth but desire to avail myself of such changes and alterations as fall within the purview of the following claims.

I claim:

1. In a method wherein a system is evacuated by means of a vapor actuated pump, the step of entraining gas in a stream of vapors of a working fluid, comprising a polyphenyl ether having at least three phenyl groups and two oxygen linkages, and at most seven phenyl groups and six oxygen linkages.

2. That method according to claim 1 wherein said working fluid essentially consists of a mixture of such polyphenyl ethers.

3. In a method wherein a system is evacuated by means of a vapor actuated pump, the step of entraining gas in a stream of vapors of a working fluid wherein said working fluid contains a polyphenyl ether having a molecular weight in the range of 264 to 641 inclusive.

4. That method according to claim 2 wherein said working fluid essentially consists of a polyphenyl ether or mixtures thereof which boil between 160° C. and 300° C. at .1 millimeter.

References Cited in the file of this patent

UNITED STATES PATENTS

2,951,629 Shepardson ---------- Sept. 6, 1960