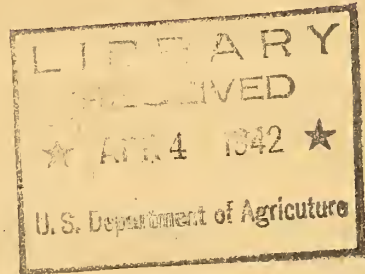


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UNITED STATES DEPARTMENT OF AGRICULTURE
BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING
U.S. REGIONAL SOYBEAN INDUSTRIAL PRODUCTS LABORATORY
Urbana, Illinois



ABSTRACTS OF ARTICLES AND PATENTS ON
MOLECULAR OR SHORT-PATH DISTILLATION

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INTRODUCTION

In connection with its work on molecular distillation of the glycerides and minor constituents of soybean oil, the U. S. Regional Soybean Industrial Products Laboratory during the fiscal years 1938-1941, inclusive, has assembled a file of patents and journal articles dealing with all phases of molecular distillation. Titles of these papers have been published previously (1, 2). In the following pages abstracts of their contents are made available to others interested in applying this valuable physico-chemical tool to research in other fields of organic chemistry.

As a matter of convenience the abstracts have been arranged in chronological order and numbered serially; similar patents have been grouped under the same serial number, chronological order of filing within the group being indicated by a, b, c, etc., after the serial number. A list of patents in numerical order under countries in alphabetical order and an alphabetical index of authors, patentees, and patent assignees, with references to abstract numbers, are appended to the list of abstracts.

The abstracts include references not only to true molecular distillation but also to short-path high-vacuum distillation since the distinction between these two types of distillation is arbitrary and certainly not critical. The following definitions adequately serve the present purpose:

1. High-vacuum distillation refers to distillation under a pressure of less than 1 mm. of mercury.
2. "Short-path high-vacuum distillation is a particular case of high-vacuum distillation and is carried out at a pressure not exceeding 10^{-2} mm. of mercury, preferably between 10^{-2} and 10^{-6} mm. of mercury, under such conditions that the vaporized molecules leaving the evaporator have direct and easy access to a condensing surface in close proximity to the evaporating surface (3)." The evaporating and condensing surfaces may be "from about half-an-inch to a few inches apart."
3. Molecular distillation is a special case of short-path distillation, in which the distance between evaporating and condensing surfaces is less than the mean free path of the molecules involved at the pressure used.

Choice of the proper pressure range and the distance between evaporating and condensing surfaces is in general dependent upon the vapor pressure, molecular weight, and thermal instability of the substances involved, and the desired rate of distillation.

Reviews of the subject generally give credit for the first application of true molecular distillation to Bronsted and Hevesy (Abstract 3), in their separation of the isotopes of mercury, although, as Washburn (Abstract 11) points out, "the rate of distillation under conditions

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analogous to those which prevail in this type of still has been employed by Langmuir and others (4) as a method for measuring the vapor pressure of metals at high temperatures." In the decade following the Brønsted-Hevesy papers, molecular distillation was independently applied to organic substances of very low vapor pressure by Waterman (Abstract 7), Purch (Abstract 8), Washburn (Abstract 11), and Hickman (Abstract 15). However, the advantages of distillation over a more or less short path had been recognized for many years prior to the work of Brønsted and Hevesy. According to Caldwell and Hurtley (Abstract 1), Chevreul (5) first showed that fats and the higher fatty acids could be distilled without decomposition in a Toricellian vacuum. Krafft and coworkers carried out a number of vacuum distillations of fats and fatty acids (6) and in some of their later work apparently approached molecular conditions; for example, they showed that lauric, myristic, palmitic, and stearic acids would sublime at a measurable rate even at ambient temperatures. Other early applications of short-path vacuum distillation are mentioned in the abstracts.

Except for the Brønsted-Hevesy papers, articles on the high-vacuum sublimation of metals have not been abstracted. A list of such papers by Chaudron and coworkers is appended on page 89.

A statement giving useful information on patents, and in particular directions for obtaining specifications and drawings, is given on page ii of Chemical Abstracts, Vol. 35 No. 1 (January 10, 1941).

As long as they are available, additional copies of this mimeographed publication may be obtained without cost upon application to the U. S. Regional Soybean Industrial Products Laboratory, Urbana, Illinois.

Literature Cited

- (1) Detwiler and Markley. Oil and Soap 16, 2-5 (1939).
- (2) Detwiler. Oil and Soap 17, 241-243 (1940).
- (3) Fawcett. British patent 501,194.
- (4) Jones, Langmuir, and Mackay. Phys. Rev. 30, 201 (1927), and the literature there cited. Also Knudsen. Ann. Phys. 47, 697 (1915).
- (5) Chevreul. Les Corps Gras, pp. 23, 77, 178, 186.
- (6) Krafft, et al. Ber. 29, 1316, 2240; 32, 1623; 33, 3207; 36, 1690, 4339, 4344; 37, 95; 38, 242, 254, 262; 40, 4770, 4775, 4779; 42, 202, 210.

ABSTRACTS OF PATENTS AND JOURNAL
ARTICLES RELATING TO MOLECULAR DISTILLATION

1. Caldwell, Kenneth S., and Hurtle, William Holdsworth
J. Chem. Soc. 95, 853 (1909)

THE DISTILLATION OF BUTTER FAT, COCOANUT OIL, AND THEIR FATTY ACIDS

Flasks of 50-300 cc. capacity were used, having a trap in the neck 2 to 6 cm. above the bulb of the flask, and a receiver tube leading from the trap. A cathodic vacuum was obtained with a Caede pump, and was estimated by means of a Crookes tube. Heat was supplied by an alloy or paraffin bath.

Fatty acids from coconut oil were distilled at temperatures much lower than those previously reported by Krafft using ordinary vacuum distillation apparatus, e.g., lauric 89°, myristic 98°, palmitic 114°, stearic 128°, oleic 130°. At a slower rate the distillations could have been carried out at even lower temperatures. "In the vacuum of the cathode light a liquid has no boiling point, but ... sublimes or evaporates, just as water does in air below its boiling point, at a rate and at a temperature depending on the nature of the substance and on the temperature to which it is heated." Similar distillations were carried out on fatty acids from butter, and on triglycerides from butter and coconut oil.

2. Bömer, A., and Baumann, J.
Z. Unters. Nahrge.-u. Genussm. 40, 97 (1920)
Issue of Sept. 15, 1920

BEITRÄGE ZUR KENNNTNIS DER GLYCERIDE DER FETTE UND ÖLE. IX. DIE GLYCERIDE
DES COCOSFETTES

Coconut oil, in 70-80 g. portions, was distilled in the vacuum produced by a Krafft falling mercury pump. The distillation flask was apparently of the Anschütz type, i.e., having an enlarged (sausage) side-arm for the collection of distillate. Most of the distillate was removed in the temperature range 255 to 260°C. Distillation was carried out under high-vacuum, short-path, non-ebullient conditions, although it is doubtful that an uninterrupted path obtained between distilling and condensing surfaces.

The essentials of this paper were presented orally by Bömer at the meeting of the Association of German Nutrition Chemists at Coblenz, May 23, 1914 (see Z. Unters. Nahrge.-u. Genussm. 28, 586 (1914); Chem. Z. 38, 844 (1914)).

53. Brönsted, J. N., and Hevesy, G. von
Nature 106, 144 (1920)

Dated September 23, 1920; issue of September 30, 1920

THE SEPARATION OF THE ISOTOPES OF MERCURY

Partial separation of the isotopes of mercury was accomplished by molecular distillation in a small pot-type still. In one experiment one-seventh of a charge of 40 cm.³ of mercury was evaporated and condensed on a highly cooled surface; the condensate had a density of 0.999980, taking the density of ordinary mercury as unity. In another experiment about three-fourths of the mercury was evaporated and the residual portion examined; its density was 1.000031. Densities were measured with a pycnometer, with an error of less than one part in a million.

4. Volmer, M.
Z angew. Chem. 34, 149 (1921)

Received for publication March 31, 1921; issue of April 15, 1921

NEUE HOCHVAKUUMMETHODEN IN DER CHEMIE

Short-path sublimations can be carried out at pressures around .01 mm. in a cylindrical distillation flask having an internal condenser. Suspended below the condenser are four trays for the reception of distillate fractions, each tray being supported from "ears" on the tray next above. The outer wall and bottom of each tray acts as a condenser for the reception of distillate in the tray next below. Distillation is rapid and non-ebullient. In an example, 25 cc. of o- and p-nitrotoluene (b.p. 220° and 237° resp. at 760 mm.) were distilled in 15 minutes at a bath temperature of 35°.

5. Brönsted, J. N., and Hevesy G. von
Nature 107, 619 (1921)

Dated June 29, 1921; issue of July 14, 1921

THE SEPARATION OF THE ISOTOPES OF CHLORINE

Concentrated hydrochloric acid cooled to -50°C. was fractionated under high vacuum in a pot-type molecular still, the distillate being condensed on a surface cooled with liquid air. The lightest and heaviest fractions were converted to sodium chloride. Densities of the salt from these fractions were 1.20222 and 1.20235, respectively, at 20°C. These figures corresponded to a difference of 6.5 percent in the atomic ratio of the isotopes of chlorine.

- 6a. ["]Brönsted, J. N., and Hevesy, G. von
Z. physik. Chem. 99, 189 (1921)

Dated June 1921; received for publication August 29, 1921

["]ÜBER DIE TRENNUNG DER ISOTOPEN DES QUECKSILBERS

The theory of molecular distillation is discussed in its application to a partial separation of the isotopes of mercury. A pot-type molecular still is described and illustrated, having a capacity of 300 cm.³ and a distance between evaporating and condensing surfaces of 1 to 2 cm. The condensing dome is cooled with liquid air. Under the vacuum produced by a Vollmer pump and at 45°C. (vapor pressure of mercury 0.01 mm., mean free path ca. 10 mm.), the distillation rate was 0.35 cm.³ per hour per cm.² of evaporating surface. Under such conditions a definite separation of mercury isotopes was achieved, as measured by density determinations. Separation was effected even at higher temperatures, e.g., 120°C., when the vapor pressure was 0.7 mm., the mean free path 0.15 mm., and the distillation rate 1.5 cm.³ per hour per cm.². Two similar stills, having capacities of 40 and 8 cm.³ of distilland, are described.

The experimental results confirm the assumption that the rate of molecular distillation of the components of a mixture is inversely proportional to the square root of the molecular weights of these components.

Isotope separation was also achieved by effusion methods.

- 6b. ["]Brönsted, J. N., and Hevesy, G. von
Phil. Mag. (6) 43, 31 (1922)
Issue of January, 1922

ON THE SEPARATION OF THE ISOTOPES OF MERCURY

An English translation of the foregoing paper.

7. Waterman, H. I., and Nijholt, J. A.
Chem. Weekblad 24, 268 (1927)
Dated April, 1927

DESTILLATIE VAN COCOSOLIE BIJ ZEER LAGEN DRUK

Previous apparatus for the high-vacuum (with mercury vapor pump) distillation of coconut oil (Waterman and Rijks, Z. deut. Öl-Fett-Ind. 46, 177 (1926) was modified to include a distillation flask containing an internally water-cooled condenser which permitted molecular distillation. Coconut oil distilled with the modified apparatus at free air (McLeod gage) pressures of 0.002 - .003 mm., was suitable for edible purposes; the chemical constants remained unaltered, and there was no decomposition.

This work was apparently the first application of truly short-path high-vacuum distillation to the purification of organic substances. It seems to have been done without knowledge of the work of Brønsted and Hevesy on isotopes of mercury and chlorine.

- 8a. Burch, Cecil R., Bancroft, Frank E., and Metropolitan-Vickers Electrical Company, Ltd.
British patent 303,078
Applications September 21, 1927 and March 12, 1928
Complete spec. accepted December 21, 1928

IMPROVEMENTS IN OR RELATING TO VACUUM DISTILLATION

The invention relates to the evaporative vacuum distillation of organic materials at the lowest temperatures consistent with reasonable speed of operation, whereby thermal decomposition and formation of azeotropic mixtures are avoided. A distilland is heated within a highly evacuated chamber (i.e., molecules of residual gas have been substantially removed) and distillate molecules are collected on a cooled condensing surface located at a distance from the distilland surface which is commensurate with the mean free path of the distillate molecules. For substances of very low vapor pressure which distill quietly, without ebullition, the distilland surface-condenser gap may be less than this mean free path. More volatile substances which splash when distilling require the interposition of heated baffles between distilling and condensing surfaces, so that distillate molecules reach the condenser by diffusion over a longer path.

Metal apparatus for large-scale distillations is described and illustrated. A vacuum-tight chamber contains a series of superimposed horizontal trays over which the distilland flows; residue from one tray is passed to the tray next below. About 1 cm. above each distilling surface is placed an inclined condenser for the collection of distillate; drainage gutters from the condensers may be arranged to collect one or several fractions in the course of a single distillation. Apparatus incorporating baffles for use in ebullient distillations is also shown. Pressures of the order of 10^{-3} mm. are obtained with a condensation pump.

A complete continuous distilling plant is described.

Several examples show the application of molecular distillation to petroleum products.

Six claims cover the process of molecular distillation of organic materials in the several types of apparatus mentioned. Two claims cover distillates and residues so obtained.

- 8b. Burch, Cecil R., and Bancroft, Frank E. (to Associated Electrical Industries, Ltd.)
U. S. patent 1,955,321
Application August 22, 1928
In Great Britain September 21, 1927
Patented April 17, 1934

VACUUM DISTILLATION

Corresponds to British patent 303,078 with the addition of two figures of modified apparatus and several paragraphs of text. Apparatus for both ebullient and non-ebullient vacuum distillation is described and illustrated. Two claims cover "a process of distilling liquid organic material that is subject to thermal decomposition comprising vaporizing the material at sub-atmospheric pressure and condensing the distillate upon a surface that is situated at a distance from the surface of the distilland less than the mean free path of a molecule of the distillate vapor."

- 8c. Metropolitan-Vickers Electrical Co.
French patent 662,643
Application August 16, 1928
Prior applications in Great Britain September 21, 1927 and March 12, 1928
Granted March 25, 1929
Published August 9, 1929

PERFECTIONNEMENTS AUX DISTILLATIONS DANS LE VIDE

Corresponds to British patent 303,078 and U. S. patent 1,955,321. Nine claims cover the molecular distillation of organic materials in the different types of apparatus described, and materials obtained by use of the process.

- 8d. Burch, Cecil R., Bancroft, Frank E., and Metropolitan-Vickers Electrical Co., Ltd.
British patent 303,079
Application Sept. 21, 1927 (Divided out of No. 303,078)
Complete spec. accepted Dec. 21, 1928

IMPROVEMENTS IN OR RELATING TO VACUUM DISTILLATION

The five claims cover molecular stills for carrying out the non-ebullient distillations described in British 303,078.

8e. Burch, Cecil R., Bancroft, Frank E., and Associated Electrical Industries, Ltd.

British patent 315,186

Application July 19, 1928 (Divided out of No. 303,078)

Complete spec. accepted July 11, 1929

IMPROVEMENTS IN OR RELATING TO VACUUM DISTILLATION

The five claims cover molecular stills similar to those of British 303,079, but modified to include the features of an internal condensation pump. Part or all of the molecules distilling from the horizontal evaporating surfaces, diffuse through a narrow passage, acquiring enough velocity to entrain and eject molecules of residual gas in the space above the evaporating surfaces. The residual gas is then removed by the pumps, while the organic distillate molecules are condensed on the walls of the still chamber.

8f. Metropolitan-Vickers Electrical Co.

German patent 580,213

Apparently similar to British 315,186. Patent not at hand.

8g. Associated Electrical Industries, Ltd.

Polish patent 11,592

Application August 16, 1928

Prior applications in Great Britain September 21, 1927 and March 12, 1928

Granted January 28, 1930

SPOSÓB DESTYLACJI PRÓŻNIOWEJ I URZĄDZENIE DO WYKONYWANIA TEGO SPOSOBU
(Process and Apparatus for Vacuum Distillation.)

Similar to British patents 303,078 and 303,079. Eight claims.

9. Müller, Alex

Proc. Roy. Soc. A120, 437 (1928)

Received for publication June 20, 1928; issue of September 1, 1928

A FURTHER X-RAY INVESTIGATION OF LONG CHAIN COMPOUNDS (n-HYDROCARBON)

For purifying the hydrocarbon $C_{30}H_{62}$, a small distillation apparatus was built in which minute quantities of the substance could be distilled in a vacuum on to a polished surface. This apparatus, a pot-type molecular still, is described in detail by Gilchrist and Karlik (Abstract 30).

- 10a. Hickman, K.
J. Opt. Soc. Am. 18, 62 (1929)
Dated July 31, 1928; issue of January 1929

A SUBLIMATION MERCURY STILL.

Pure mercury is prepared by vacuum sublimation from an electrically-heated alembic. Mercury evaporated under the vacuum produced by a Hyvac pump is condensed on the rounded dome of the alembic, draining into an annular trough and thence into a collecting vessel. A battery of the alembics may be set up to operate in series.

- 10b. Hickman, K.
J. Soc. Chem. Ind. 48, 366 (1929)
Issue of April 12, 1929

A SUBLIMATION MERCURY STILL.

Same as foregoing reference.

11. Washburn, Edward W., Bruun, Johannes H., and Hicks, Mildred M.
J. Res. Nat. Bur. Standards 2, 467 (1929) (Research Paper RP 45)
Dated August 4, 1928; presented before Am. Chem. Soc., September, 1928; issue of March, 1929

APPARATUS AND METHODS FOR THE SEPARATION, IDENTIFICATION, AND DETERMINATION OF THE CHEMICAL CONSTITUENTS OF PETROLEUM

The paper contains descriptions of a rectifying still with a 20-plate column, all-glass rectifying stills for vacuum distillation, apparatus for low-temperature fractional crystallization, apparatus for combustion analysis, and various types of molecular stills. The latter are of the pot type and are improved modifications of those described by Bronsted and Hevesy.

Essential features of a molecular still comprise a high vacuum (equal to or better than the vapor pressure of the substance at the temperature of distillation), a large and clean area of evaporating surface, a short distance between the evaporating surface and the condenser, and a sufficient temperature difference between the distilling surface and the condensing surface (not less than 60° for organic compounds to be distilled at room temperatures). It is pointed out that under efficient cooling conditions, the distillation rate of a given molecular species in a molecular still may be calculated by means of the Langmuir equation

$$n = pS \sqrt{\frac{1}{2\pi MRT}}$$

where n is the number of mols of the substance distilling per second, p its vapor pressure at the evaporating surface at $T^\circ\text{K}$., S the effective area in cm^2 , M the molecular weight, and R the gas constant in ergs. Azeotropic mixtures may in general be separated in molecular stills, since the rate of evaporation of a given molecular species is determined not only by its partial vapor pressure but by its molecular weight.

Experiments were carried out on the molecular distillation of mercury, paraffin wax, calomel, and sucrose.

12. Waterman, H. I., and Elsbach, E. B.
Chem. Weekblad 26, 469 (1929)
Dated September, 1928; issue of Sept. 21, 1929

TOESTEL VOOR HET UITVOEREN VAN DESTILLATIES ONDER ZEER LAGEN DRUK.

In this improvement of a previous distillation flask (Abstract 7), a condenser terminates immediately above the liquid in the distillation flask. The condensate drops into a tube conducted up through the bottom of the flask and flows into a multiple receiver, which is immersed in liquid air and connected with a high-vacuum pump. Connections are made with ground joints. The apparatus is illustrated. As an example, α -bromonaphthalene (b. 281.1° at 760 mm.) was readily distilled in the present apparatus at a pressure of a few thousandths of a mm. and a temperature of 50° ; slow distillation occurred even at $18-20^\circ$.

13. Burch, C. R.
Nature 122, 729 (1928)
Issue of Nov. 10, 1928

OILS, GREASES, AND HIGH VACUA

By distillation of petroleum in a molecular still of the Brønsted and Hevesy type, an oil of very low vapor pressure (e.g., 10^{-3} mm. at 118°C .) was obtained. When used as working fluid in a condensation pump, without artificial cooling, this oil gave results comparable with the performance of a mercury vapor pump having a cold trap 100°C . below room temperature. When ionization gages were evacuated with pumps using such oil, pressures of 7.5×10^{-7} mm. were reached without ovening the glass; when the glass was ovened the pressure was no greater than 7.5×10^{-8} mm.

Greases (petroleum jelly residues) were also prepared from still residues, having a vapor pressure not greater than 7.5×10^{-4} mm. at 320°C . and less than 7.5×10^{-7} mm. at 70°C .

14. Burch, C. R.

Proc. Roy. Soc. (London) A123, 271 (1929)

Received for publication Jan. 29, 1929; issue of March 6, 1929

SOME EXPERIMENTS ON VACUUM DISTILLATION.

In this paper are described in detail the previously noted experiments (Abstract 13) on the molecular distillation of petroleum products. The apparatus, adapted from that of Bronsted and Hevesy, includes a horizontal electrically-heated copper tray having a surface area of 40 cm.² and a capacity of 30 cm.³ of distilland. Surrounding this tray is a water-cooled condenser having a surface area of 200 cm.² placed at a slight angle to the horizontal; a spout at the lower end of the condenser leads to a multiple receiver. The condenser is evacuated by a mercury condensation pump without the use of a cold trap. Temperatures are measured by a thermocouple soldered to the evaporating tray, and pressures are estimated by means of a high-tension discharge.

Detailed discussions of degassing technique and the distillation process are presented. To show temperature reductions permitted by molecular distillation, a petroleum residue from atmospheric distillation at 320° was separated in the molecular still into a fraction evaporating over the range 112-250° (yield 55 percent, mean molecular weight 498) and a fraction evaporating over the range 250-314° (yield 25 percent, molecular weight 801). The molecular weight of the residue was 1550. Other examples are cited. Distillates were obtained which were suitable for use as working fluids in condensation pumps.

5a. Hickman, K.

J. Opt. Soc. Am. 18, 69 (1929)

Issue of January 1929

A STILL FOR LIQUIDS OF HIGH BOILING POINT

Thermal decomposition makes difficult the ordinary vacuum distillation of high-boiling liquids, such as butyl phthalate, to be used for lubricating the walls of manometer tubes. The difficulties can be overcome by use of a short-path distillation apparatus, following the general principles set forth by Bronsted and Hevesy, and by Washburn. Because volatile impurities are present in crude organic liquids, high vacua cannot be attained, but satisfactory operation occurs at pressures produced by a Hyvac pump.

The still is a modification of the alembic described for the distillation of mercury (Abstract 10a). Several receivers attached to the annular trough permit removal of several fractions during a single distillation, by altering the angle of support of the alembic.

- 15b. Hickman, K.
J. Soc. Chem. Ind. 48, 365 (1929)
Issue of April 12, 1929

A STILL FOR LIQUIDS OF HIGH BOILING POINT.

Same as foregoing reference.

16. Eastman Kokak Co.
Synthetic Organic Chemicals 2, No. 3 (1929)
Issue of February, 1929

TACKLING DIFFICULT DISTILLATIONS.

The technique described by Hickman (Abstract 15a) has been extended so that such complex substances as castor oil may be distilled, or rather sublimed, without appreciable loss. After a preliminary degassing to remove most of the dissolved air and volatile impurities, the substance is placed in an electrically-heated alembic similar to that previously described and subjected to distillation. Temperatures of the distilland are measured by a thermometer suspended from the top of the alembic and sealed thereto by a rubber connection. For heavy paraffin hydrocarbons and aromatic acids and esters, distillation can take place under the vacuum of a Hyvac oil pump. For substances of less volatility or thermal stability (e.g., dibenzyl malonate, tolyl benzene, or anthracene oils), a Langmuir condensation pump is used in series with the backing pump. For vegetable oils or triglycerides a trap cooled with dry ice may be placed between pumps and still.

- 17a. N. V. de Bataafsche Petroleum Maatschappij
Dutch patent 27,023
Application February 27, 1930
Application published August 15, 1931
Dated May 7, 1932
Published June 15, 1932

WERKWIJZE EN INRICHTING TOT HET UITVOEREN VAN DESTILLATIES BIJ ZEER LAGEN DRUK.

A molecular still is described and schematically illustrated, which consists of an evacuated chamber containing a number of heated vertical plates over which a liquid distilland flows by gravity in a thin film. Similar cooled plates serve as condensers for the distillate. Since the distilland flows over both sides of each evaporating plate, distillate molecules escape to the condensers on either side; but the plates are paired in such a manner that the distance from a given evaporator to the condenser in the direction of the pump, is several times longer than the distance to the condenser in the other direction. Both distances are of the order of the mean free path of the distillate molecules. The net

effect is that the distillate molecules, driving along with them the molecules of noncondensable gas, serve to propel the latter at molecular velocities in the direction of the pump. This feature and the provision of thin films of distilland are essential for efficient distillation.

Four claims for the process and apparatus.

- 17b. N. V. de Bataafsche Petroleum Maatschappij
German patent 608,253
Application January 14, 1931
Prior application in Holland February 27, 1930
Granted December 27, 1934
Published January 19, 1935

VORRICHTUNG ZUM DESTILLIEREN IM HOCHVAKUUM

Corresponds to Dutch patent 27,023.

- 17c. N. V. de Bataafsche Petroleum Maatschappij
British patent 358,391
Application January 22, 1931
Convention date (Holland) February 27, 1930
Complete spec. accepted October 3, 1931

PROCESS AND APPARATUS FOR CARRYING OUT DISTILLATIONS UNDER LOW PRESSURE

Corresponds to Dutch patent 27,023. Four claims for process and apparatus.

- 17d. N. V. de Bataafsche Petroleum Maatschappij
French patent 709,974
Application January 26, 1931
Prior application in Holland February 27, 1930
Granted May 26, 1931
Published August 17, 1931

PROCÉDÉ ET APPAREIL DE DISTILLATION SOUS PRESSION RÉDUITE

Corresponds to Dutch patent 27,023. Four claims for process and apparatus.

- 17e. van Dijck, Willen J. D. (to N. V. de Bataafsche Petroleum Maatschappij)
Australian patent 863/31
Application February 23, 1931
Prior application in the Netherlands February 27, 1930
Complete specification accepted February 23, 1932
Acceptance advertised March 3, 1932

PROCESS AND APPARATUS FOR CARRYING OUT DISTILLATIONS UNDER LOW PRESSURE

Similar to Dutch patent 27,023. Four claims for apparatus and process.

- 18. Hickman, K. C. D., and Sanford, C. R.
 J. Phys. Chem. 34, 637 (1930)
 Issue of March 1930

THE PURIFICATION, PROPERTIES, AND USES OF CERTAIN HIGH-BOILING ORGANIC LIQUIDS

The paper gives a comprehensive account of molecular distillation problems encountered in an investigation of high-boiling liquids suitable for lubricating mercury manometers. (See also Abstracts 15a and 16.) While the alembics previously described are suitable for the sublimation of liquids of moderate volatility, special apparatus and technique are required for distilling substances of low vapor pressure or thermal stability. The use of organic liquids such as butyl phthalate and butyl benzyl phthalate to replace mercury in condensation pumps, is suggested, and a pump to operate with these liquids is described.

- 19. Carothers, Wallace H., Hill, Julian W., Kirby, James E., and Jacobson, Ralph A.
 J. Am. Chem. Soc. 52, 5279 (1930)
 Received for publication October 9, 1930; published December 18, 1930

STUDIES ON POLYMERIZATION AND RING FORMATION. VII. NORMAL PARAFFIN HYDROCARBONS OF HIGH MOLECULAR WEIGHT PREPARED BY THE ACTION OF SODIUM ON DECAMETHYLENE BROMIDE

High molecular weight paraffins, prepared by coupling dibromides with sodium, were fractionated in a small pot-type molecular still of the Washburn design (Abstract 11) having a surface area of 18 cm.². The (free air) pressure was maintained below 10⁻⁶ mm. Eighteen fractions, comprising 50 percent of the distilland, were collected at temperatures between 130 and 300°C. These distillates were grouped into eight fractions and redistilled, and the new distillates crystallized to constant melting point. The fractions so treated varied in melting point from 35 to 105°C. and in composition from C₂₀H₄₂ to C₇₀H₁₄₂.

- 20. Hickman, Kenneth C. D. (to Eastman Kodak Co.)
 U. S. patent 1,925,559
 Application December 23, 1930
 Patented September 5, 1933

VACUUM EXTRACTION OF COD-LIVER OIL

A cod-liver oil fraction of high therapeutic efficacy is obtained by molecular distillation in a column still at temperatures between 100 and 200°C. and pressures of the order of .001 mm. Degassed oil is allowed to flow in a thin film over a column heated internally by a refluxing liquid or by electrical means. Distillate is condensed on an outer jacket surrounding the evaporating surface at a distance between 1 and .001 in. and flows into an annular trough at the bottom of the still, whence it drains into a receiving flask. Another receiver is provided for undistilled residues. Two claims cover the process of vacuum extraction of cod-liver oil or therapeutic constituents thereof.

21. Hickman, Kenneth C. D. (to Eastman Kodak Co.)
U. S. patent 1,942,858
Application December 23, 1930
Patented January 9, 1934

DISTILLATION APPARATUS

The patent covers apparatus for vacuum distillation of difficultly volatile liquids. Included are the column molecular still described in U. S. patent 1,925,559 (above) and a multiple still for stepwise distillations. The latter comprises a series of nested columns; the outer surface of a given column acts as the evaporator for one evacuated chamber, while the inner surface of the same column acts as the condenser for the chamber next within, and so on. Undistilled residues are pumped from the bottom of one chamber to the evaporating surface of the chamber next within. A source of heat within the innermost column provides a downward gradation of temperature at each evaporating surface from the inside out. Four claims for apparatus.

22. Hickman, K.
J. Franklin Inst. 213, 119 (1932)
Presented at the meeting of February 18, 1931; dated November 4, 1931;
issue of February 1932

A VACUUM TECHNIC FOR THE CHEMIST

This detailed review of vacuum technique includes discussions of the theory of ordinary and molecular distillation, as well as descriptions and illustrations of various types of stills, pressure gages, condensation pumps, and vacuum assemblies.

23. Carothers, Wallace H. (to E. I. du Pont de Nemours and Co.)
U. S. patent 2,071,250
Application July 3, 1931
Patented February 16, 1937

LINEAR CONDENSATION POLYMERS

Linear condensation polymers are prepared from substances having two functional groups, by heating the reaction mixture in a pot-type molecular still to remove volatile nonpolymerized components. The still is that described by Carothers and Hill (Abstract 25). The 28 claims cover the use of molecular distillation for preparing linear polymers, and the polymers thus prepared.

24. Carothers, Wallace H. (to E. I. du Pont de Nemours and Co.)
U. S. patent 2,071,251
Original application July 3, 1931 (divided out of No. 2,071,250)
New application March 14, 1933; renewed September 10, 1936
Patented February 16, 1937

FIBER AND METHOD OF PRODUCING IT

Linear condensation polymers are prepared by treatment in a molecular still as shown in U. S. patent 2,071,250 (above). Such products can be formed into fibers said to be strong, pliable, and having permanent orientation along the fiber axis. Thirty-five claims for synthetic fibers and the method of drawing them.

25. Carothers, Wallace H., and Hill, Julian W.
J. Am. Chem. Soc. 54, 1557 (1932)
Received for publication November 12, 1931; published April 6, 1932

STUDIES OF POLYMERIZATION AND RING FORMATION. XI. THE USE OF MOLECULAR EVAPORATION AS A MEANS FOR PROPAGATING CHEMICAL REACTIONS

Molecular distillation permits completion of reversible bifunctional polymerizations by removal of volatile or semi-volatile condensation products.

A Washburn type pot still, modified to permit ready access to the working parts, is described and illustrated. The apparatus is inclosed within two hemispheres having an equatorial greased joint between them. Over an electrically-heated glass evaporating tray is placed a flattened water-cooled condensing bulb. Temperatures are measured with a thermocouple. Support tubes for condenser and evaporating tray are sealed to the hemispheres by rubber stoppers coated with wax.

It is estimated that the upper limit of molecular distillation for paraffin hydrocarbons may begin at molecular weights between 1100 and 1200.

26. Carothers, Wallace H., and Hill, Julian W.
J. Am. Chem. Soc. 54, 1559 (1932)
Received for publication November 12, 1931; published April 6, 1932

STUDIES OF POLYMERIZATION AND RING FORMATION. XII. LINEAR SUPERPOLY-ESTERS

Molecular stills of the Washburn type provide means for continuously displacing physical equilibria involving very minute vapor pressures. In an example, the trimethylene ester of hexadecamethylene dicarboxylic acid was placed in the still and heated at 200° for 12 days. During the first seven days a small amount of distillate collected on the condenser, while no distillate was observed during the remaining five days. The viscosity of the residual polyester increased progressively during the heating, and the final product showed an apparent molecular weight of about 12,000. A part of the effect of the molecular still treatment is evidently due to the greatly prolonged time of heating.

27. Carothers, Wallace H., and Hill, Julian W.
J. Am. Chem. Soc. 54, 1566 (1932)

Received for publication November 12, 1931; published April 6, 1932

STUDIES OF POLYMERIZATION AND RING FORMATION. XIII. POLYAMIDES AND MIXED POLYESTER-POLYAMIDES

A polyamide was placed in the molecular still and heated for 48 hours at 200°. A small amount of crystalline cyclic lactam distilled from the reaction mixture, and the residue was considerably changed in its properties. It was harder and tougher than before and in thin sections was flexible and elastic.

28. Hill, Julian W., and Carothers, Wallace H.
J. Am. Chem. Soc. 54, 1569 (1932)

Received for publication November 12, 1931; published April 6, 1932

STUDIES OF POLYMERIZATION AND RING FORMATION. XIV. A LINEAR SUPERPOLYANHYDRIDE AND A CYCLIC DIMERIC ANHYDRIDE FROM SEBACIC ACID

The α -sebacic anhydride prepared by the action of acetic anhydride or acetyl chloride on sebacic acid is polymeric. When heated in the molecular still two simultaneous changes occur: the α -anhydride is transformed into a polyanhydride of much higher molecular weight (the ψ -anhydride), which remains in the still residue, and at the same time depolymerization occurs with the formation of a crystalline product (β -anhydride) which is shown to be the 22-membered cyclic dimer; this dimer is distilled and collected on the condensing surface of the still. At its melting point the dimer reverts to a higher polymer (γ -anhydride).

29. Carothers, Wallace H., and Kirby, James E.
J. Am. Chem. Soc. 54, 1588 (1932)

Received for publication November 12, 1931; published April 6, 1932

STUDIES OF POLYMERIZATION AND RING FORMATION. XVI: A POLYALCOHOL FROM DECAMETHYLENE DIMAGNESIUM BROMIDE

A polyalcohol was prepared from decamethylene dimagnesium bromide by treatment of the di-Grignard with methyl formate. A sample of the polyalcohol, melting at 110-113°, was heated at 150° in the molecular still under a pressure less than 10^{-5} mm. A trace of crystalline solid of melting point 80° collected on the condenser, which was within 1 cm. of the evaporating surface. The residue was a colorless, semitransparent, tough, pliable mass, insoluble in the common solvents, and was probably a three-dimensional polymer.

30. Gilchrist, Helen S., and Karlik, Berta
J. Chem. Soc. 1932, 1992
Received for publication Feb. 17, 1932

SEPARATION OF NORMAL LONG-CHAIN HYDROCARBONS BY FRACTIONAL DISTILLATION IN HIGH VACUUM

The molecular still of Müller (Abstract 9) was used to separate mixtures of eicosane ($C_{20}H_{42}$) and triacontane ($C_{30}H_{62}$) at pressures around 10^{-4} mm. and at a maximum temperature of 70°C. X-ray analysis showed that excellent fractionation had been effected.

The apparatus is illustrated and described in detail. Distilland is placed in a small platinum crucible set into a copper block, which is heated by a platinum spiral. Directly over the crucible is a glass cover slip mounted on the end of a hollow copper tube; since the latter is filled with a dry ice mixture, any distillate is condensed on the cover slip. By means of two ground joints the apparatus may readily be opened for the introduction of samples or removal of distillate fraction. The still is connected to a mercury vapor pump through a cold trap. Pressures are estimated by means of a high-tension discharge.

31. Freudenberg, Karl, Friedrich, Karl, Bumann, Ilse, and Soff, Karl
Ann. 484, 41 (1932)
Received for publication February 27, 1932

ÜBER LIGNIN UND CELLULOSE. XVIII. ÜBER CELLULOSE UND STÄRKE

A pot-type molecular still was used for the distillation of a tetrasaccharide. The horizontal outer casing and inner condensing tube, made from quartz cylinders, are fitted with a ground joint at one end. The other end of the outer cylinder is connected to a liquid air trap and mercury vapor pump. The condenser tube is cooled with water or a dry ice mixture. The distilland is placed on the floor of the outer tube, which is heated in an air bath.

32. Heilbron, I. M., Heslop, R. N., Morton, R. A., Webster, E. T., Rea, J. L., and Drummond, J. C.
Biochem. J. 26, 1178 (1932)
Received for publication May 17, 1932

CHARACTERISTICS OF HIGHLY ACTIVE VITAMIN A PREPARATIONS

To increase the potency of vitamin A concentrates from halibut oil, high vacuum sublimation was employed. A vitamin concentrate was placed in a boat at the end of a horizontal tube 1 meter long. This tube is divided by constrictions into segments and is surrounded by an electric furnace capable of graded heating, usually 150°-20°. The far end of the tube is connected by a ground joint to a liquid air trap and mercury vapor pump. Pressures are estimated by a high-frequency discharge.

A vitamin concentrate was sublimed at 150-155° for 3-1/2 hours, at pressures below 10^{-4} mm. The largest fraction (49 percent) was a golden yellow oil which condensed in the segment heated to 80-110°. Spectrophotometric evidence showed that some changes had occurred in this apparently undecomposed concentrate, since sharp maxima (at 297, 313.5, 330, 348, 368, 393 m μ .) were superimposed upon the customary broad absorption curve of vitamin A (max. at 328 m μ .).

With the collaboration of Carr and Jewell of British Drug Houses, the distillation of rich halibut and other liver oil concentrates was also carried out in a new type of molecular still (not described), wherein rapid fractional distillation could be effected at pressures below 10^{-5} mm. Under these conditions the vitamin distilled without decomposition or molecular change, giving a main fraction evaporating at 137-8° which had a considerably enhanced potency. $E_{1\text{cm}}^{1\%}$ for the best preparation was 1370 at 328m μ , while the antimony trichloride blue value was 65,000.

33. Burch, Cecil R., Preece, Frederick H., and Associated Electrical Industries, Ltd.
British patent 396,205
Application June 9, 1932
Complete spec. accepted August 3, 1933

IMPROVEMENTS IN AND RELATING TO HIGH VACUUM DISTILLATION SYSTEMS

A heated trap is placed between a molecular still and the rotary pump so that organic vapors from the system, instead of fouling the pump, will be decomposed into "solid and noncondensable gaseous ingredients".

34. Hill, Julian W.
Science 76, 218 (1932)
Issue of September 2, 1932

THE "MOLECULAR STILL" AS A TOOL OF BIOCHEMICAL RESEARCH

A brief discussion of the principles and applications of the molecular still. In the author's laboratory glucose, sorbitol, and glycine have been distilled unchanged without difficulty at good rates at temperatures 50 or more degrees below their melting points. It is probable that any substance can be distilled unchanged if the heat of dissociation of its least stable bond is greater than the molecular cohesion.

- 35a. Imperial Chemical Industries, Ltd.
Dutch patent 35,201
Application December 20, 1932
Application published November 15, 1934
Dated March 16, 1935
Published April 15, 1935

WERKWIJZE EN INRICHTING VOOR HET VERWIJDEREN VAN LAGERMOLECULAIRE
BESTANDDELEN UIT DOOR POLYMERISATIE VAN DROGENDE OLIËN VERFREGEN
PRODUCTEN, DOOR EVENTUEEL CONTINU UITGEVOERDE DESTILLATIE IN VACUO

Low molecular weight non-polymerized glycerides and free fatty acids are removed from stand oils by molecular distillation in a column still. The still consists of a vertical electrically-heated inner tube closed at the upper end, which serves as an evaporating surface. Distilland is flowed over this tube in a thin film. Distillate is condensed on the wall of a concentric outer tube which is cooled by a water jacket, and flows into an annular trough, thence into a receiver. Three claims for process and apparatus.

- 35b. Oosterhof, Dirk, van Vlodrop, Cornelus, and Waterman, Hein I. (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,065,728
Application December 16, 1932
In the Netherlands December 20, 1932
Patented December 29, 1936

PROCESS FOR REMOVING LOW MOLECULAR GLYCERIDES FROM POLYMERIZED OILS BY
DISTILLATION

Similar to Dutch patent 35,201. Ten claims for the distillation process.

- 35c. Imperial Chemical Industries, Ltd.
British patent 422,941
Application December 20, 1933
Convention date (Holland) December 20, 1932
Complete spec. accepted January 22, 1935

IMPROVEMENTS IN THE DISTILLATION OF POLYMERISED DRYING OILS

Similar to Dutch patent 35,201. Seven claims for apparatus, process, and products obtained thereby.

35d. Imperial Chemical Industries, Ltd.

German patent 643,993

Application December 20, 1933

Prior application in Holland December 20, 1932

Granted April 1, 1937

Published April 22, 1937

VERFAHREN ZUR VERBESSERUNG DER EIGENSCHAFTEN VON STANDOLEN

Similar to Dutch patent 35,201. Two claims

36. Carr, Francis H., and Jewell, William

Nature 131, 92 (1933)

Dated January 10, 1933; issue of January 21, 1933

CHARACTERISTICS OF HIGHLY ACTIVE VITAMIN A

Highly active vitamin A preparations were obtained by use of a molecular still. This still had an evaporating surface of 30 cm.² and a distance between evaporating and condensing surfaces of 1.2 cm. Pressures within the apparatus were of the order of 10^{-5} mm. By raising the temperature in 5-7° increments, separative distillation was effected over the range 115-170°C. The fraction removed at 136-137° was adjudged to be a purer vitamin A than any thitherto described. $E_{1\%}^{1\text{cm}}$ at 328 m μ . was 1600, while the antimony trichloride blue value was 78,000.

37a. British Drug Houses, Ltd., Carr, F. H., and Jewell, W.

British patent 415,088

Application January 17, 1933

Complete spec. accepted August 17, 1934

IMPROVEMENTS IN OR RELATING TO THE DISTILLATION OF LIQUIDS CONTAINING VITAMINS

Liver oils are subjected to molecular distillation at pressures between .01 and .0001 mm. to obtain a distillate having a high content of vitamins, particularly vitamins A and D. A suitable molecular still assembly is illustrated; it includes a degassing chamber and two or more column stills arranged for gravity flow of the residue from the bottom of one column to the top of the next column, which can be maintained at a higher temperature. U-traps between the different units permit them to be maintained at successively lower pressures. Twelve claims for apparatus, process, and vitamin concentrates obtained thereby.

- 37b. British Drug Houses, Ltd., Carr, Francis H., and Jewell, William
French patent 767,191
Application January 16, 1934
Prior application in Great Britain January 17, 1933
Granted May 1, 1934
Published July 12, 1934

PERFECTIONNEMENTS AU TRAITEMENT DES PRODUITS NATURELS CONTENANT DES
VITAMINES

Similar to British patent 415,088. Ten claims for process and apparatus.

- 37c. British Drug Houses, Ltd., Carr, Francis H., and Jewell, William
German patent 670,016
Application January 17, 1934
Prior application in Great Britain January 17, 1933
Granted December 15, 1938
Published January 10, 1939

VERFAHREN UND VORRICHTUNG ZUR HERSTELLUNG VON VITAMINKONZENTRATEN

Similar to British patent 415,088. Three claims.

38. Imperial Chemical Industries, Ltd.
Dutch patent 37,435
Application February 23, 1933
Application published September 16, 1935
Dated January 17, 1936
Published February 15, 1936

WERKWIJZE VOOR HET BEREIDEN VAN EEN CONCENTRAAT VAN VITAMINEN EN VERWANTE
STOFFEN, IN HET BIJZONDER PROVITAMINEN, UIT NATUURPRODUCTEN EN SYNTHETISCHE
PRODUCTEN, DOOR DESTILLATIE IN VACUO

Concentrates of vitamins and related materials, as well as provitamins (ergosterol, carotene) are obtained by molecular distillation of natural and synthetic materials at pressures between .01 and .0001 mm. The products may be dissolved in olive oil, peanut oil, coco butter, etc., and used in foods, medicaments, or livestock rations. A water-jacketed electrically-heated column molecular still is illustrated, having three receivers along its length for the collection of separate fractions during a single operation. Two claims.

39. Waterman, H. I. and Oosterhof, D.
Rec. trav. chim. 52, 895 (1933) (In English)
Dated March 1933; received for publication July 17, 1933; issue of
October 15, 1933

POLYMERISATION OF LINSEED OIL

A column molecular still is described in which the evaporating surface is a vertical glass tube, internally heated by an electrical element. Oil, previously degassed in an overhead reservoir, is allowed to drip onto the outer surface of this tube, which is frosted to assure an evenly-distributed thin film of distilland. Any distillate is condensed on the inner surface of a water-cooled outer jacket, flowing into an annular trough and thence to a receiver. Undistilled oil is collected in another receiver near the bottom of the column. The space between evaporating and condensing tubes is evacuated by a vacuum pump connected to charcoal traps immersed in liquid air. Pressures are estimated by means of a high tension discharge. Because of the short time of contact (3-4 seconds) of the distilland on the hot evaporating surface, decomposition of the oil is minimal.

In this column linseed oil was distilled at 250-60° without significant change in constants. Stand oil was similarly treated with the following results:

| | Weight grams | Molecular weight | Viscosity poises |
|------------|-----------------|---------------------|---------------------|
| Stand oil | | 1610 | 55.2 |
| Distillate | 19 | 757 | 1.51 |
| Residue | 41 | 3643 | 379.0 |

The distillate, consisting of free fatty acids and unpolymerized glycerides, became cloudy on standing and had poor drying properties. The residue, on the other hand, remained clear on standing, dried better than the original stand oil, and had a lower acid number.

- 40a. Imperial Chemical Industries, Ltd.
British patent 437,895
Application May 7, 1934
Convention date (Holland) May 9, 1933
Complete spec. accepted November 7, 1935

IMPROVEMENTS IN THE TREATMENT OF SOLIDS

By suspension of solution in a suitable liquid, solids may be distilled in a column molecular still at pressures between 10^{-2} and 10^{-5} mm. Preferably the diluent should be partly volatile at the temperature of distillation. A suitable still is that described in Dutch patent 37,435 (Abstract 38).

Examples are given of the distillation of β -aminoanthraquinone at 120° in a mineral oil diluent, and of the o-anisidide of β -oxynaphthoic acid at 200°, mixed with linseed stand oil. Other examples include caffeine and dyestuffs. Seven claims for process and materials purified thereby. (Parent Dutch patent not at hand.)

- 40b. Waterman, Hein I., and van Vlodrop, Cornelius (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,129,596
Application May 4, 1934
In the Netherlands May 9, 1933
Patented September 6, 1938

TREATMENT OF SOLIDS

Similar to British patent 437,895. Twenty-one claims for the process of distilling female sex-hormone, alkaloids, dyestuffs, etc., in the manner specified.

- 40c. Imperial Chemical Industries, Ltd.
French patent 773,068
Application May 8, 1934
Prior application in Netherlands May 9, 1933
Granted August 25, 1934
Published November 10, 1934

PROCÉDÉ ET APPAREIL POUR LA DISTILLATION DE SUBSTANCES SOLIDES

Similar to British patent 437,895. Seven claims for process and products obtained thereby.

41. Carothers, W. H., and van Natta, F. J.
J. Am. Chem. Soc. 55, 4714 (1933)
Received for publication August 8, 1933; published November 7, 1933

STUDIES OF POLYMERIZATION AND RING FORMATION. XVIII. POLYESTERS FROM w-HYDROXYDECANOIC ACID

In preparing a polyester of molecular weight 20,700, hydroxydecanoic acid was heated at 250° for 50 hours in a molecular still consisting essentially of a suction flask into which a water-cooled test tube was inserted to act as a condenser. During the first few hours a considerable amount of distillate (dimer and unchanged acid) collected on the condenser.

42. Hill, J. W., and Carothers, W. H.
J. Am. Chem. Soc. 55, 5023 (1933)

Received for publication September 2, 1933; published December 14, 1933

STUDIES OF POLYMERIZATION AND RING FORMATION. XIX. MANY-MEMBERED CYCLIC ANHYDRIDES.

α -Anhydrides were prepared by the action of acetic anhydride or acetyl chloride on pimelic, suberic, azelaic, undecanedioic, dodecanedioic, brassylic, tetradecanedioic, and octadecanedioic acids. They are all linear polymers with molecular weights between 3000 and 5000. When heated in the molecular still, they disproportionate, yielding in the distillate β -anhydrides (cyclic monomers or dimers) and in the residue ω -anhydrides (superpolymers of high molecular weight).

The molecular still, which is illustrated, is a cylindrical vessel 18 cm. high and 5 cm. in diameter, with a rather flat curved bottom and an outlet to a mercury diffusion pump backed by a Hyvac pump. Into this vessel is fitted, by means of a large ground joint at the top, another cylinder 3 cm. in diameter which served as the condenser; its rounded bottom was 3 cm. from the bottom of the outer vessel. A trap cooled by a dry ice mixture was placed in the system.

43. Hill, J. W., and Carothers, W. A.
J. Am. Chem. Soc. 55, 5031 (1933)

Received for publication September 2, 1933; published December 14, 1933

STUDIES OF POLYMERIZATION AND RING FORMATION. XX. MANY-MEMBERED CYCLIC ESTERS

When linear polyesters of unit length greater than seven are heated to 200-250° in a molecular still, the long chains couple to form still longer chains. The resultant superpolyesters have molecular weights above 10,000 and are capable of being drawn out into tough, pliable, highly oriented fibers.

The simplified still consists of a 250-cc suction filter flask into which is inserted by means of a rubber stopper a test tube 1.5 cm. in diameter which serves as a condenser. The bottom of the tube is 3 cm. above the bottom of the flask; the inside is cooled with tap water or a dry ice mixture. Vacua of 0.1 to 2 mm. are maintained. The flask is immersed in an electrically-heated metal bath.

44. Carothers, W. H., and Hill, J. W.
J. Am. Chem. Soc. 55, 5043 (1933)

Received for publication September 2, 1933; published December 19, 1933

STUDIES OF POLYMERIZATION AND RING FORMATION. XXII. STEREOCHEMISTRY AND MECHANISM IN THE FORMATION AND STABILITY OF LARGE RINGS

The thermalysis of thorium octadecanedioate was investigated as carried out by Ruzická. During this reaction a linear polymer -- a polyketone -- is formed; if this is heated in the molecular still, it cracks and gives appreciable amounts of the monocyclic ketone. The still is not described.

45. van Katta, F. J., Hill, J. W., and Carothers, W. H.
J. Am. Chem. Soc. 56, 455 (1934)
Received for publication October 20, 1933

STUDIES OF POLYMERIZATION AND RING FORMATION. XXIII. ϵ -CAPROLACTONE AND ITS POLYMERS

To test its susceptibility to depolymerization the linear polyester of ϵ -caprolactone (molecular weight about 4000) was heated for 90 hours at 250° in a molecular still, under a pressure of 1 to 2 mm. Only a small amount of distillate was collected -- a viscous, dark-colored oil containing a few crystals of the cyclic dimer. The polymeric residue was darker in color but otherwise apparently unchanged.

46. Washburn, Edward W.
American Petroleum Inst. Proc. 14th Ann. Meeting, Sect. III, 111 (1933)
Presented October 26, 1933

CHEMICAL CONSTITUENTS OF PETROLEUM -- A. P. I. RESEARCH PROJECT 6

In connection with the isolation and identification of the hydrocarbon constituents of petroleum, various types of new or improved apparatus have been developed, including molecular stills for distillation in extreme vacuum. (See abstract 11).

- 47a. Imperial Chemical Industries, Ltd., Fawcett, Eric W., and Walker, Eric F.
British patent 442,000
Application November 24, 1933
(Patent of addition to British 422,941 (Abstr. 35c))
Complete spec. accepted January 31, 1936

DRYING OILS

Polymerized fish oils (menhaden, Japanese sardine, Canadian pilchard, etc.) are subjected to molecular distillation as in British patent 422,941, to remove unpolymerized constituents. The residue has superior properties as a paint or varnish ingredient. Three claims for process and oils produced thereby.

- 47b. Imperial Chemical Industries, Ltd.
German patent 658,844
Application November 18, 1934
Prior application in Great Britain November 24, 1933
Granted March 24, 1938
Published April 20, 1938

VERFAHREN ZUR VERBESSERUNG VON STABDOLEN AUS FISCHOLEIN

Similar to British patent 442,000. Two claims.

- 47c. Fawcett, Eric W., and Walker, Eric F. (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,128,354
Application November 22, 1934
In Great Britain November 24, 1933
Patented August 30, 1938

DRYING OIL

Similar to British patent 442,000. Ten claims for process and oil produced thereby.

- 47d. Canadian Industries, Ltd. (assignee of E. W. Fawcett and E. E. Walker)
Canadian patent 378,403
Filed January 21, 1936
Granted December 20, 1938

DRYING OIL

Similar to British patent 442,000. Eight claims.

- 47e. Imperial Chemical Industries, Ltd.
Belgian patent 406,148

Apparently similar to British patent 442,000. Patent not at hand.

- 48a. Waterman, Hein I., and van Vlodrop, Cornelus
Dutch patent 43,250
Application December 16, 1933
Application published August 15, 1936
Dated April 21, 1938
Published May 16, 1938

WERKWIJZE TER BEREIDING VAN KOEKBAKKERIJPRODUCTEN EN VAN BOTERVETDESTILLAAT
TEN GEBRUIKE HIERBIJ

Butterfat is passed through a column molecular still at pressures between

.1 and .001 mm. and at temperatures between 180 and 240°, to obtain a distillate rich in flavor and vitamin content, suitable for use in cooking. The residue is suitable for shortening, margarine, etc.

- 18b. Waterman, Hein I., and van Vlodrop, Cornelus (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,144,900
Application December 11, 1934
In the Netherlands December 16, 1933
Patented January 24, 1939

FLAVORING MATTERS AND THEIR APPLICATION

Similar to Dutch patent 43,250. Thirteen claims for process and preparations obtained thereby.

- 18c. Imperial Chemical Industries, Ltd.
British patent 448,800
Application December 14, 1934
Convention date (Netherlands) December 16, 1933
Complete spec. accepted June 15, 1935

FLAVOURING MATTERS OBTAINED FROM BUTTER FAT AND THEIR APPLICATION

Similar to Dutch patent 43,250. Five claims for process and preparations obtained thereby.

- 18d. Imperial Chemical Industries, Ltd.
French patent 782,731
Application December 14, 1934
Prior application in Netherlands December 16, 1933
Granted March 25, 1935
Published June 11, 1935

MATIÉRES SAPORIFIQUES ET LEUR APPLICATION

Similar to Dutch patent 43,250. Four claims for process and products obtained thereby.

- 18e. Waterman, Hein I., and van Vlodrop, Cornelus (to Imperial Chemical Industries, Ltd.)
Australian patent 20,902/35
Application January 11, 1935
Complete specification accepted October 22, 1935
Acceptance advertised October 31, 1935

FLAVOURING MATTERS, AND THEIR APPLICATION

Similar to Dutch patent 43,250. Six claims for process and product.

- 49a. Bancroft, Frank E. and Associated Electrical Industries, Ltd.
British patent 428,719
Application February 28, 1934
Complete spec. accepted May 17, 1935

IMPROVEMENTS IN VACUUM DISTILLATION APPARATUS

The invention comprises a metal column molecular still having a number of distilling units within a single evacuated chamber. Each evaporating surface is surmounted by a tiered distributor which distributes the distilland around the upper edge of the evaporating surface in a uniform thin film. Ten claims for apparatus.

- 49b. Metropolitan-Vickers Electrical Co., Ltd. (assignee of Frank E. Bancroft)
Canadian patent 362,459
Filed January 22, 1936
Granted December 8, 1936

VACUUM DISTILLATION APPARATUS

Similar to British patent 428,719. Thirteen claims.

- 50a. Fawcett, Eric W., McCowen, John L., and Imperial Chemical Industries, Ltd.
British patent 434,726
Application March 7, 1934
Complete spec. accepted September 9, 1935

IMPROVEMENTS IN AND RELATING TO VACUUM DISTILLATION

A molecular distillation apparatus contains a number of units in a common vacuum chamber; each unit comprises a vertical distilling surface heated internally and a coaxial condensing surface. Temperatures of the distilling or condensing surfaces, or both, may be adjusted independently. By means of electromagnetic pumps, distillates and residues are transferred from one unit to another, in a stated order, to obtain the maximum fractionation of the constituents of the distilland. Four claims for apparatus.

- 50b. Fawcett, Eric W., and McCowen, John L. (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,073,202
Application March 7, 1935
In Great Britain March 7, 1934
Patented March 9, 1937

VACUUM DISTILLATION

Similar to British patent 434,726. Three claims for apparatus.

- 51a. Fawcett, Eric W., McCowen, John L., and Imperial Chemical Industries, Ltd.
British patent 455,032
Application March 7, 1934
Complete spec. accepted September 9, 1935

IMPROVEMENTS IN AND RELATING TO THE VACUUM DISTILLATION OF MATERIALS YIELDING A SOLID DISTILLATE OR RESIDUE

In the molecular distillation of materials yielding a solid distillate or residue the solid may be removed from evaporating or condensing surfaces by a scraper in the form of a piston ring traversing the surface by means of a screw, for delivery to a receiver. Modifications for vertical and horizontal stills are described. The apparatus may be used in distilling caffeine from coffee beans, quinine from quachia bark, crude β -aminoanthraquinone, etc. Nine claims for apparatus and process.

- 51b. Fawcett, Eric W., and McCowen, John L. (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,109,129
Application July 30, 1936
In Great Britain March 7, 1934
Patented February 22, 1938

APPARATUS FOR HIGH VACUUM DISTILLATIONS

Similar to British patent 455,032. Eight claims for apparatus and process.

52. Waterman, H. I., and Elsbach, E. E.
Rec. trav. chim. 53, 731 (1934) (in English)
Received for publication March 29, 1934

THE QUANTITATIVE STUDY OF THE OXIDATION OF CITRONELLAL

Citronellal readily oxidizes even at room temperature to form peroxides, citronellic acid, and carbon dioxide. The reaction mixture, after removal of citronellic acid, can be molecularly distilled to separate peroxides from unaltered citronellal.

53. Waterman, H. I., Over, J., and Tulleners, A. J.
Rec. trav. chim. 53, 699 (1934) (in English)
Received for publication March 11, 1934

POLYMERISATION OF ISOBUTENE

Isobutene obtained from isobutanol was polymerized with an aluminum chloride catalyst at low temperatures. The end product fractionated in a molecular still.

54. Waterman, H. I., and van Vlodrop, C.
Rec. trav. chim. 53, 670 (1934) (in English)
Received for publication March 27, 1934

DIFFERENCES BETWEEN BIOLOGICALLY ACTIVE SUBSTANCES BEFORE AND ISOLATION FROM THE RAW MATERIAL IN WHICH THEY OCCUR

Carotene dissolved in palm oil can be recovered in concentrated form without decomposition, by molecular distillation in a column still (Abst. 39). However, the red pigments of natural palm oil, while distillable, are not preferentially concentrated by molecular distillation. When distillates from natural palm oil are redistilled it becomes possible to concentrate the pigments. It is surmised that for the most part carotene does not occur as a free molecule in natural palm oil.

55. van der Hulst, L. J. N.
Rec. trav. chim. 53, 672 (1934) (in English)
Received for publication March 29, 1934

PRELIMINARY NOTES ON THE APPLICATION OF ABSORPTION SPECTRA IN OIL RESEARCH: DISTILLATION OF PALM OIL

The conclusions by Waterman and van Vlodrop (above) have been confirmed by absorption spectra measurements of natural palm oil and a solution of carotene in bleached palm oil, comparing each with its molecular distillate and distillation residue.

Fawcett, Eric W., and Imperial Chemical Industries, Ltd.
British patent 438,056
Application May 11, 1934
Complete spec. accepted November 11, 1935

PROCESS OF REFINING CRUDE FATS AND FATTY OILS

Molecular distillation is effective for purifying fats and oils if first the oil is treated with a small amount of alkali to remove "break" material. The breaking step is necessary prior to distillation, partly because it avoids mechanical troubles which might be caused by the presence of mucilage in the short path still, but more so because it appears to assist the distillation in some way, at present not fully understood, as evidenced by the superior yield and quality of the final product. This is a remarkable effect in view of the very small quantities of breaking substances which may

be used." Eight claims for the process and refined oils obtained thereby; vitamin-containing liver oils are excepted.

- 56b. Imperial Chemical Industries, Ltd.
French patent 789,919
Application May 11, 1935
Prior application in Great Britain May 11, 1934
Granted August 26, 1935
Published November 8, 1935

PERFECTIONNEMENTS AU RAFFINAGE DES GRAISSES ET DES HUILES GRASSES BRUTES

Similar to British patent 438,056. Six claims for process and product.

- 6c. Canadian Industries, Ltd. (assignee of Eric W. Fawcett)
Canadian patent 378,404
Filed January 31, 1936
Granted December 20, 1938

FAT AND OIL REFINING PROCESS

Similar to British patent 438,056. Sixteen claims.

57. Breusch, Fritz
Z. physiol. Chem. 227, 242 (1934)
Received for publication July 28, 1934

NEUE METHODE DER GALLINANALYSE

Fatty acids were removed from a bile saponification mixture by distillation in a simplified molecular still at 150° under a vacuum of 0.2 mm. The apparatus consists of a cylindrical suction flask in which is mounted, by means of a rubber stopper, a water-cooled condenser. Heat is supplied by a metal or oil bath.

- 8a. Waterman, Hein I., van Dijk, Johannes A., and Imperial Chemical Industries, Ltd.
British patent 452,442
Application February 21, 1935
Complete spec. accepted August 21, 1936

IMPROVEMENTS IN AND RELATING TO THE TREATMENT OF VITAMIN-CONTAINING OILS AND PRODUCTS OBTAINED THEREFROM

Vitamin-containing oils are subjected to mild hydrogenation and molecular distillation, in either order, to obtain odorless and tasteless concentrates suitable for incorporation into foodstuffs and medicaments. The extent of

hydrogenation depends upon the type of product desired. In an example, cod-liver oil was hydrogenated (60-70°, 120 atmospheres) with a nickel catalyst to give a paste-like mass having a blue value (Carr-Price reaction for vitamin A) of 5.6. Molecular distillation at 180° and 10⁻³ mm. gave 8 percent of a tasteless and odorless distillate having a blue value of 40. Six claims for process and products obtained thereby.

58b. Waterman, Hein, I., and van Dijk, Johannes A. (to Imperial Chemical Industries, Ltd.)

U. S. patent 2,143,587

Application February 20, 1936

In Great Britain February 21, 1935

Patented January 10, 1939

TREATMENT OF VITAMIN-CONTAINING OILS AND PRODUCTS OBTAINED THEREFROM

Similar to British patent 452,442. Six claims for process and products.

58c. Imperial Chemical Industries, Ltd.

French patent 802,177

Application February 21, 1936

Prior application in Great Britain February 21, 1935

Granted June 6, 1936

Published August 29, 1936

PERFECTIONNEMENTS AU TRAITEMENT DES HUILES CONTINANT DES VITAMINES ET PRODUITS EN RESULTANT

Similar to British patent 452,442. Five claims for process and products.

Hill, J. W., and Carothers, W. H.

J. Am. Chem. Soc. 57, 925 (1935)

Received for publication March 21, 1935

STUDIES OF POLYMERIZATION AND RING FORMATION. XXIV. CYCLIC AND POLYMERIC FORMALS

Linear or α -polymers prepared by the action of glycols on formals, were heated in a simplified molecular still of the type previously described (Abstract 43). The temperature of heating was 230-250°, the pressure about 1 mm. After 48 hours a distillate was collected which proved to be the solid cyclic dimer mixed with the liquid monomer. The residue, a hard opaque mass, was a linear superpolymer of molecular weight up to 20,000.

60. Fawcett, Eric W., and Imperial Chemical Industries, Ltd.
British patent 457,120
Application May 21, 1935
Complete spec. accepted November 23, 1936

IMPROVEMENTS IN OR RELATING TO APPARATUS FOR VACUUM DISTILLATION

The molecular still described is intended especially for use in low-temperature distillations where the condensing surface must be cooled to below room temperature. A refrigerant can be circulated through a jacket surrounding the condensing tube. Outside of the refrigerating jacket is a second jacket which, being connected to the distilling chamber, can be evacuated to the same extent thereas, and hence forms an insulation for the refrigerating jacket. Four claims for apparatus.

61. Vigers, Brian E. A., and Imperial Chemical Industries, Ltd.
British patent 457,778
Application June 4, 1935
Complete spec. accepted December 4, 1936

IMPROVEMENTS IN OR RELATING TO HIGH VACUUM DISTILLATION APPARATUS

To secure a molecular still in which the component parts are leakproof and resistant to distortion, the invention provides for evaporating and/or condensing surfaces formed by a massive body of good conducting metal (e.g., aluminum) cast around seamless metal tubing (e.g., steel or copper) adapted for the passage of heating or cooling media. Three claims for apparatus.

62. Markley, K. S., Hendricks, Sterling B., and Sando, Charles E.
J. Biol. Chem. 111, 133 (1935)
Received for publication June 8, 1935; issue of September 1935

CONSTITUENTS OF THE WAX-LIKE COATING OF THE PEAR, PYRUS COMMUNIS, L.

Crude nonacoasne, $C_{29}H_{60}$, was distilled in a Washburn-Mair pot-type molecular still at a temperature of 150° with a free air pressure below 2.5×10^{-4} mm. Although no appreciable change in temperature was observed during the distillation, two fractions were cut. The distillation effected some separation of a higher hydrocarbon which was present in small amounts, but did not affect oxygenated impurities which were, however, completely removed by subsequent treatment with sulfuric acid.

- 63a. Vigers, Brian E. A., McCowen, John L., and Imperial Chemical Industries, Ltd.
British patent 458,117
Application June 14, 1935
Complete spec. accepted December 14, 1936

IMPROVEMENTS IN AND RELATING TO APPARATUS FOR HIGH VACUUM DISTILLATION

An improved molecular still is described which permits ready access to the interior and working parts of the apparatus with a minimum of vacuum joints. Narrow rectangular plates or blocks serve as the evaporating and condensing surfaces; these plates are supported in a vertical or inclined position by means of a cantilever truss attached to an end plate. The whole assembly, including the evacuating pumps, is inclosed by a horizontal cylindrical casing which makes a vacuum-tight joint with the end plate. Distilland is fed to the distilling surfaces by trough integral therewith, these troughs being supplied from other troughs to insure even distribution. Residues and distillates are collected in two series of troughs. Nine claims for apparatus.

- 63b. Vigers, Brian E. A., and McCowen, John L. (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,137,553
Application June 15, 1936
In Great Britain June 14, 1935
Patented November 22, 1938

APPARATUS FOR HIGH-VACUUM DISTILLATION

Similar to British patent 458,117. Seven claims for apparatus.

- 63c. Imperial Chemical Industries, Ltd.
French patent 815,150
Application December 17, 1936
Granted April 5, 1937
Published July 6, 1937

PERFECTIONNEMENTS AUX APPAREILS POUR LA DISTILLATION SOUS UN VIDE POUSSÉ

Similar to British patent 458,117. Eight claims for apparatus.

64. Vigers, Brian E. A., and Imperial Chemical Industries, Ltd.
British patent 458,118
Application June 14, 1935
Complete spec. accepted December 14, 1936

IMPROVEMENTS IN OR RELATING TO HIGH-VACUUM DISTILLATION APPARATUS

In designing molecular stills, greater pumping efficiency is achieved by mounting the condensation pumps within the evacuated distillation chamber. The hot parts of the pumps may be insulated by radiation screens of bright metal foil. Three claims for apparatus, which do not cover the arrangement of pumps described in British patent 458,117.

- 65a. Vigers, Brian E. A., and Imperial Chemical Industries, Ltd.
British patent 458,119
Application June 14, 1935
Complete spec. accepted December 14, 1936

IMPROVEMENTS IN OR RELATING TO HIGH-VACUUM DISTILLATION AND APPARATUS THEREFOR

A molecular still for the distillation of solid materials is described. The apparatus is contained within a vacuum-tight horizontal cylindrical chamber. Evaporating and condensing surfaces are formed by parallel moving surfaces spaced a short distance apart; these surfaces may be formed by thin endless metal belts. Stationary heating and cooling elements are mounted at the rear of these belts. Solid distilland is fed from hoppers into the chamber through a suitable regulating valve, and is evenly distributed in a thin layer on the evaporating surface. Distillate and residue are removed from the belts by scrapers and deposited in separate collecting hoppers. Seven claims for process and apparatus.

- 65b. Vigers, Brian E. A. (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,073,327
Application June 15, 1936
In Great Britain June 14, 1935
Patented March 9, 1937

HIGH VACUUM DISTILLATION AND APPARATUS THEREFOR

Similar to British patent 458,119. Six claims for process and apparatus.

- 65c. Imperial Chemical Industries, Ltd.
French patent 807,351
Application June 15, 1936
Prior application in Great Britain June 14, 1935
Granted October 12, 1936
Published January 11, 1937

PERFECTIONNEMENTS À LA DISTILLATION À VIDE ÉLEVÉ ET AUX APPAREILS UTILISÉS À CET EFFET

Similar to British patent 458,119. Six claims for process and apparatus.

65d. Imperial Chemical Industries, Ltd.
German patent 643,877

Apparently similar to British patent 458,119. Patent not at hand.

65e. Imperial Chemical Industries, Ltd. (B. E. A. Vigers, inventor)
Swedish patent 90,721

Application June 12, 1936

Prior application in Great Britain June 14, 1935

Accepted September 9, 1937

Published November 9, 1937

SÄTT OCH ANORDNING FÖR KOFTVÄGIG HÖGVARUUNDESTILLATION

Similar to British patent 458,119. Five claims.

66a. Hickman, Kenneth C. D. (to Eastman Kodak Co.)
U. S. patent 2,126,466

Application August 24, 1935

Patented August 9, 1938

MEDICINAL OLFEANINOUS DISTILLATION

Unsaturated animal or vegetable oils are subjected to molecular distillation as described in previous patents (Abstracts 20 and 21) to obtain a distillate of unsaturated glycerides free of protein material, free fatty acids, incipient rancidity, and objectionable odor, and suitable for use in foods. Nine claims for process.

66b. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 485,549

Application August 18, 1936

Convention date (United States) August 24, 1935

Complete spec. accepted May 18, 1938

IMPROVED PROCESS OF DISTILLATION OF NATURAL GLYCERIDES AND PREPARATION OF VITAMIN COMPOSITIONS

Similar to U. S. patent 2,126,466. Six claims for process and materials produced thereby.

6c. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 485,614

Application August 18, 1936 (divided out of British 485,549)

Convention date (United States) August 24, 1935

Complete spec. accepted May 18, 1938

IMPROVED PROCESS OF DISTILLATION OF LINSEED AND SIMILAR OILS

Unbroken linseed and similar oils are subjected to molecular distillation as described in previous patents (Abstracts 20 and 21). A "late" distillate fraction constituting a highly purified oil is collected, which is more unsaturated than the initial material and is suitable for use as a "super" drying oil. The treatment of broken or otherwise refined oils is disclaimed. One process claim.

- 66d. Eastman Kodak Co.
French patent 809,700
Application August 22, 1936
Prior application in United States August 24, 1935
Granted December 12, 1936
Published March 8, 1937

PROCÉDÉ DE TRAITEMENT DES SUBSTANCES OLÉAGINEUSES ET PRODUITS EN RÉSUULTANT

Similar to U. S. patent 2,126,466. Fifteen claims for process and products thereby obtained.

67. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,205,925
Application August 24, 1935
Patented June 25, 1940

FAT SOLUBLE VITAMIN CONCENTRATE

By molecular distillation as described in previous patents concentrates of vitamins A and/or D can be obtained from fats and oils substantially entirely in their natural ester form. Three claims for compositions of matter.

68. Strain, William H., and Allen, Willard M.
Ind. Eng. Chem., Anal. Ed. 7, 443 (1935)
Received for publication August 29, 1935; issue of November 15, 1935

A MOLECULAR STILL

A small pot-type molecular still is described and illustrated. The outer jacket is a glass cylinder 22 cm. long and 5 cm. in diameter, divided into two sections by a well-ground equatorial joint. A water-cooled condensing tube having a flattened bulb at the lower end is connected by a ring seal to the upper section of the jacket. At the bottom of the lower section of the jacket is a well 3 cm. in diameter which will accomodate 1 to 2 g. of distilland. The condensing bulb is 3-1/2 cm. above the bottom of the well. A vacuum of 2×10^{-4} mm. is attained by use of a mercury vapor pump with dry ice trap.

The still has been successfully used for the purification of progesterin and other biological substances.

69. Bancroft, Frank E., and Metropolitan-Vickers Electrical Co., Ltd.
British patent 457,292
Application September 16, 1935
Complete spec. accepted November 25, 1936

IMPROVEMENTS IN VACUUM DISTILLATION APPARATUS

An improvement to molecular distillation apparatus such as that described in British patent 428,719. (Abstract 49a), in which the stills are provided with shields covering or inclosing parts over which the distilland flows on its course to the vaporizing surface so as to prevent distillation of volatile portions of the distilland except under short-path conditions. Four claims for apparatus.

70. Waterman, H. I., and van Vlodrop, C.
Chimie et industrie 34, 1056 (1935)
Presented at 5th Congr. of Ind. Chem., Brussels, September 22-28, 1935

LA POLYMERISATION ET QUELQUES APPLICATIONS DANS L'INDUSTRIE ORGANIQUE

Application of molecular distillation in apparatus previously described showed that polymerized linseed oils (stand oils) frequently have a higher iodine value than the corresponding distillates and residues. This is explained by the presence in the polymerized oil of volatile unsaturated decomposition products.

71. Mair, Beveridge J., Schicktanz, Sylvester T., and Rose, Frank W., Jr.
J. Res. Nat. Bur. Standards 15, 557 (1935) (Research Paper RP 849)
Dated October 8, 1935; issue of December 1935

APPARATUS AND METHODS FOR INVESTIGATING THE CHEMICAL CONSTITUTION OF LUBRICATING OIL, AND PRELIMINARY FRACTIONATION OF THE LUBRICATING-OIL FRACTION OF A MIDCONTINENT PETROLEUM

Included are a column molecular still and a pot-type still which are described and illustrated. The column still, constructed entirely of pyrex glass, operates on the same principle as that of Waterman and Oosterhof (Abstract 39). The evaporating surface is provided by a column 2 cm. in diameter and about 100 cm. long. Heat is supplied by refluxing a high-boiling kerosene within this column, which is packed with jack chain; use of the kerosene instead of an electric heater prevents local superheating on the evaporating surface. The top of this reflux column is connected to a system whose pressure can be varied at will, permitting control of the distillation temperature. The composition of the kerosene is such that a temperature gradient of about 15° exists along the column. Five thermocoupl

within the column permit measurement of the temperatures of different sections. The condensing surface is constituted by an air-cooled outer tube 5 cm. in diameter. Five annular rings equally spaced along the condensing surface, and connecting to receivers, permit the simultaneous withdrawal of five distillate fractions; a sixth receiver at the bottom of the column is provided for the collection of undistilled residues. The charge of oil is placed in a 2-liter degassing and preheating flask, from which it flows by gravity through a magnetic valve, at an appropriate rate, on to the evaporating surface.

The pot still, an improvement of previous models described by Hickman and Sanford (Abstract 18), is a large cylindrical flask surmounted by an air-cooled dome which forms the condensing surface. Distillate flows down the dome into an annular ring, from which it drains into a multiple receiver; a small funnel with iron core, operated electromagnetically, is used to direct the distillate as desired into any of six small receivers. The vacuum need not be broken during distillation of the charge. The still may be constructed with a flask diameter of 12 cm. and a capacity of 1.5 liters of distilland.

- 72a. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,146,894
Application October 11, 1935
Patented February 14, 1939

VACUUM DISTILLATION

In the molecular distillation of oils containing vitamins, sterols, or hormones, temperatures considerably above the boiling point of the desired distillate must be used; e.g., vitamin A esters, pure, distill at 160-190°, but when present in the parent oil in small amounts, they distill at 180-215°. If a substance having a volatility near that of the vitamin (such as tripepalgonin) be added to the oil, this substance and the vitamin will distill out of the oil together at a temperature lower than that required for the vitamin alone. The added substance, whose bulk further aids in sweeping the solid distillate out of the system, is then separated from the vitamin by molecular distillation in a separate still, or by other known means. The process applies to the removal of sterols and hormones, as well as vitamins, from oils. Ten process claims.

- 2b. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 476,134
Application October 10, 1936
Convention date (United States) October 11, 1935
Complete spec. accepted December 2, 1937

IMPROVED PROCESS OF HIGH VACUUM DISTILLATION

Similar to U. S. patent 2,146,894. Nine process claims.

- 72c. Eastman Kodak Co.
French patent 811,766
Application October 10, 1936
Prior application in United States October 11, 1935
Granted January 23, 1937
Published April 22, 1937

PROCÉDÉ DE PURIFICATION DE MATIÈRES ORGANIQUES PAR DISTILLATION DANS LE VIDE

Similar to U. S. patent 2,146,894. Seven process claims.

- 73a. Fawcett, Eric W., Whittaker, Donald, and Imperial Chemical Industries, Ltd.
British patent 464,395
Application October 19, 1935
Complete specification accepted April 19, 1937

IMPROVEMENTS IN AND RELATING TO THE PRODUCTION OF OILS RICH IN VITAMINS

An improvement of British patent 415,088. A difficulty of past work in the concentration of vitamins in raw oils by molecular distillation, is that there is a limit to the degree of concentration of the vitamin. By the present method, the oils are first partially saponified -- to the extent of about 10 percent -- whereafter they are molecularly distilled, giving a distillate of very high vitamin content. The explanation given, in the case of vitamin A, is that on partial saponification the natural vitamin A ester is preferentially converted to vitamin A alcohol before saponification of the bulk of the oil. The free alcohol is more readily distillable than the ester. Seven claims for process and vitamin concentrates obtained thereb

- 73b. Imperial Chemical Industries, Ltd.
French patent 811,920
Application October 19, 1936
Prior application in Great Britain October 19, 1935
Granted January 23, 1937
Published April 26, 1937

PROCÉDÉ DE PRODUCTION D'HUILES RICHES EN VITAMINES

Similar to British patent 464,395. Five claims for process and product.

- 73c. Imperial Chemical Industries, Ltd.
Dutch patent 44,870
Application October 2, 1936
Application published August 15, 1938
Accepted December 16, 1938
Published January 16, 1939

WERKWIJZE VOOR HET BEREIDEN VAN VITAMINERIJKE FRACTIES VAN OLIEN

Similar to British patent 464,395. Two claims.

- 74a. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,150,683
Application October 26, 1935
Patented March 14, 1939

DISTILLATION PROCESS

Because of the presence of dissolved oxygen and peroxides, it is difficult to concentrate vitamins (e.g., vitamins A, D, E) by molecular distillation of animal and vegetable oils, because of oxidative decomposition. Decomposition is avoided by addition of an antioxidant to the oil before distillation. Thus, hydroquinone is added to a fish oil containing vitamins A and D and the oil is molecularly distilled between 90 and 200° at a pressure below .01 mm. The antioxidant should have a volatility near that of the substance whose recovery is of interest. Pyrogallol, p-aminophenol, 1, 2, 4-trihydroxybenzene, furfural, and benzyl-p-aminophenol are suitable. Thirteen process claims.

- 74b. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 480,885
Application October 17, 1936
Convention date (United States) October 26, 1935
Complete spec. accepted March 2, 1938

IMPROVEMENTS IN HIGH VACUUM DISTILLATION OF OILY MATERIALS

Similar to U. S. patent 2,150,683. Seven claims for process and composition of matter.

- 74c. Eastman Kodak Co.
French patent 812,734
Application October 26, 1936
Prior application in U. S. October 26, 1935
Granted February 8, 1937
Published May 15, 1937

PERFECTIONNEMENTS AUX PROCÉDÉS DE DISTILLATION DE MATIÈRES ORGANIQUES

Similar to U. S. patent 2,150,683. Eleven claims for process and product.

75. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,136,774
Application November 7, 1935
Patented November 15, 1938

TREATMENT OF OILS

The undesirable taste and odor of animal and vegetable oils, apparently caused by dissolved oxygen and peroxides, are not entirely removed by previous methods of molecular distillation. According to the present invention, the oil before distillation is treated with an inert gas or vapor of an easily volatilizable material in order to displace absorbed air and volatile materials; the oil is then passed in a thin film over a heated column at a pressure less than .1 mm. to remove residual gases and odoriferous materials. The apparatus is illustrated. Four process claims.

- 76a. Fraser, Ronald G. J., and Imperial Chemical Industries, Ltd.
British patent 467,028
Application date December 9, 1935
Complete spec. accepted June 9, 1937

IMPROVEMENTS IN OR RELATING TO HIGH-VACUUM DISTILLATION

An extension of the fractionating system described in British patent 434,726 (Abstract 50a). In a molecular distillation system comprising an even number of at least four distillation units, the condensates from the even-numbered units are returned to the evaporating surfaces of the preceding odd-numbered units, those from the odd-numbered units (except the first) being returned to the evaporating surfaces of the preceding odd-numbered units. The residues are transferred in the reverse direction from one unit to the next. In effect, for each single unit of the fractionating system of British 434,726, a double unit has been substituted. Nine claims for process and condensates obtained thereby.

- 76b. Fraser, Ronald G. J. (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,128,225
Application November 7, 1936
In Great Britain December 9, 1935
Patented August 30, 1938

FRACTIONAL SHORT-PATH DISTILLATION

Similar to British patent 467,028. Seven process claims.

- 77a. Hickman, Kenneth C. D., and Tischer, Arthur O. (to Distillation Products, Inc.)
U. S. patent 2,169,195
Application December 28, 1935
Patented August 8, 1939

PRODUCTION OF VITAMIN A ESTERS

Animal oils containing vitamin A in the alcohol form are molecularly distilled to obtain a concentrate of vitamin A alcohol. The alcohol is then treated with an acylating agent, preferably an unsaturated fatty acid derivative, to give a product containing vitamin A in the ester form, of improved keeping quality and therapeutic value. Seventeen claims for process and vitamin A esters.

- 77b. Eastman Kodak Co.
German patent 664,745
Application August 20, 1936
Prior applications in United States August 24 and December 28, 1935
Granted August 18, 1938
Published September 5, 1938

VERFAHREN ZUR HERSTELLUNG VON VITAMIN-A-PRÄPARATEN

Similar to U. S. patent 2,169,195. Two process claims.

- 77c. Eastman Kodak Co.
French patent 825,406
Application August 24, 1936
Prior applications in United States August 24 and December 28, 1935
Granted December 8, 1937
Published March 3, 1938

PROCÉDÉ DE TRAITEMENT DE VITAMINES ET PRODUITS EN RÉSULTANT

Similar to U. S. patent 2,169,195. Twenty-two claims.

- 77d. Kodak Ltd. (assignee of Eastman Kodak Co.)
British patent 481,189
Application August 5, 1936
Complete spec. accepted March 7, 1938

IMPROVEMENTS IN THE MANUFACTURE OF ESTERS

Concentrates of vitamin A alcohol, which may be obtained from natural oils by molecular distillation or by saponification, are esterified with a halide or anhydride of an unsaturated fatty acid, such as oleic or linoleic. The resultant product is said to have superior therapeutic and keeping qualities. Seven claims for process.

78. Fawcett, Eric W., and Imperial Chemical Industries, Ltd.
British patent 469,425
Application January 24, 1936
Complete spec. accepted July 26, 1937

IMPROVEMENTS IN OR RELATING TO SHORTPATH HIGH-VACUUM DISTILLATION

In molecular distillation processes, very volatile vapors present in the distilland or derived from its decomposition may cause difficulties in the pumping system by not condensing on the condensing surface; such vapors may be removed by scrubbing them with a non-volatile solvent. The scrubbing column is usually placed between the first and second condensation pumps vapors expelled from the still are dissolved in a film of oil flowing over the surface of the scrubbing column. Six claims for process and apparatus.

- 79a. Hickman, Kenneth C. D., and Hecker, John C. (to Eastman Kodak Co.)
U. S. patent 2,126,467
Application January 31, 1936
Patented August 9, 1938

DISTILLATION PROCESS

The removal of distillates (e.g., vitamins, sterols) from the condensing surface of a molecular still is sometimes difficult because of their solid or viscous nature. According to the present invention, such distillates are collected and swept out of the still by a stream of low vapor-pressure liquid which is recirculated over the condensing surface. This liquid should be miscible but nonreactive with the distillate. Laboratory and multistage pilot plant apparatus is described. Ten process claims.

- 79b. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman and John C. Hecker)
British patent 487,697
Application January 29, 1937
Convention date (United States) January 31, 1936
Complete spec. accepted June 24, 1938

IMPROVEMENTS IN HIGH VACUUM DISTILLATION PROCESS

Similar to U. S. patent 2,126,467. Five process claims.

- 79c. Eastman Kodak Co.
French patent 817,036
Application January 30, 1937
Prior application in United States January 31, 1936
Granted May 15, 1937
Published August 24, 1937

PROCEDE DE DISTILLATION

Similar to U. S. patent 2,126,467. Twenty claims for process and apparatus.

80. McDonald, Ellice
J. Franklin Inst. 221, 103 (1936)
Issue of January 1936

SOME NEW AND UNIQUE APPARATUS FOR BIOCHEMICAL STUDY

Descriptions of unusual instruments used by the Biochemical Research Foundation of the Franklin Institute are presented; they include an echelon cell, all-quartz microscope, movie camera adapted for short wavelengths of light, photoelectric quantum counter, and high-vacuum distillation apparatus. Under the latter heading is given a resume of the principles of vacuum distillation and a sketch of the pot-type molecular still in use. In this still the condenser tube, which is cooled with water or dry ice, is fitted to the outer jacket by means of a ground joint. The flattened bottom of the condenser is placed 2 to 3 mm. from the bottom of the jacket. Heat is provided by refluxing liquids placed in a flask surrounding the lower portion of the jacket. Pressures of less than 10^{-6} mm. are readily maintained by a two-stage mercury diffusion pump together with a dry ice trap.

A number of solids have been purified in the still, including glucose and sucrose; simple amino acids such as glycine, glycine anhydride, and lysine dihydrochloride; the dipeptide leucyl-glycine; ascorbic acid (175°); 1:2:5:6-dibenzanthracene (240°); chrysene; and cholesterol (100°).

81. Waterman, H. T., and Leendertse, J. J.
Trans. Faraday Soc. 32, 251 (1936)
Issue of January 1936

POLYMERIZATION OF UNSATURATED HYDROCARBONS

Molecular distillation was used to separate fractions of different molecular weight in connection with a study of the polymerization of ethylene under high pressure at $125-150^{\circ}$ with aluminum chloride as catalyst and pentane as liquid diluent; isobutene with aluminum oxide on silica gel at -40° to 40° ; pentene with aluminum chloride; hexadecane with boron trifluoride at $10-15^{\circ}$ and aluminum chloride at $17-23^{\circ}$; and cyclohexene at 70° . The apparatus is not described.

82. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman and Arthur C. Tischer)
British patent 489,023
Application January 29, 1937
Convention date (United States) February 6, 1936
Complete spec. accepted July 29, 1938

IMPROVEMENT IN HIGH VACUUM DISTILLATION OF MATERIALS CONTAINING STEROLS AND RELATED COMPOUNDS

Compounds having a cholane nucleus (sterols, saponins, and bile acids) are separated by molecular distillation from raw materials such as animal and vegetable oils and waxes, fungoid growths, etc. Six process claims. (Parent U. S. patent not at hand.)

- 82b. Eastman Kodak Co.
French patent 825,973
Application February 6, 1937
Prior application in United States February 6, 1936
Granted December 27, 1937
Published March 18, 1938

PROCÉDÉ DE DISTILLATION MOLECULAIRE

Similar to British patent 489,623. Ten claims.

- 83a. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,165,378
Application February 15, 1936
Patented July 11, 1939

VACUUM DISTILLATION

In the molecular distillation of vegetable and animal oils, etc., a liquid of low vapor pressure is added to the distilland to prevent the formation of solid or viscous residues which would clog the still. Such added liquids should be freely flowing, not subject to decomposition, and of lower vapor pressure than the distillate it is expected to obtain. Suitable substances are glycerides such as castor oil and olein, phthalates such as benzyl, butyl, amyl, and octyl phthalate, alcohols such as mono-, di-, and tri-glycerol, esters such as triacetin, methyl oleate, and methyl stearate, and high-boiling hydrocarbons such as lubricating oil. Eight process claims.

- 83b. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 490,433
Application February 15, 1937
Convention date (United States) February 15, 1936
Complete spec. accepted August 15, 1938

IMPROVEMENTS IN PROCESSES OF HIGH VACUUM-SHORT PATH DISTILLATION

Similar to U. S. patent 2,165,378. Seven process claims.

- 83c. Eastman Kodak Co.
French patent 825,974
Application February 15, 1937
Prior application in United States February 15, 1936
Granted December 27, 1937
Published March 18, 1938

PROCÉDÉ DE DISTILLATION DANS LE VIDE

Similar to U. S. patent 2,165,378. Thirteen process claims.

- 84a. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,150,684
Application February 21, 1936
Patented March 14, 1939

DISTILLATION OF SOLIDS

Solid materials may be molecularly distilled to recover constituent oils, therapeutic agents, etc. In one type of suitable apparatus, the dried and ground solid is held between two porous travelling bands and passed through a series of evacuated vessels, where the condensate is collected. The bands may travel at different speeds, to agitate the solid, and may be electrically heated. Other forms of apparatus are also described. Eight process claims.

- 84b. Eastman Kodak Co.
French patent 825,978
Application February 20, 1937
Prior application in United States February 21, 1936
Granted December 27, 1937
Published March 18, 1938

PROCÉDÉ DE DISTILLATION DE MATIÈRES SOLIDES

Similar to U. S. patent 2,150,684. Eleven claims for process, apparatus, and products obtained therewith.

- 84c. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 488,878
Application February 20, 1937
Convention date (United States) February 21, 1936
Complete spec. accepted July 15, 1938

IMPROVED PROCESS OF HIGH VACUUM DISTILLATION

Similar to U. S. patent 2,150,684, but does not cover all of the apparatus modifications described therein. Eight claims for process and apparatus.

- 85a. Hickman, Kenneth C. D. (to Eastman Kodak Co.)
U. S. patent 2,113,302
Application March 5, 1936
Patented April 5, 1938

PROCESSES OF DISTILLATION

To facilitate the molecular distillation of an organic liquid, there is added to the distilland a colored indicator which distills in maximum amounts at a temperature having a known definitely predetermined relation to that particular temperature at which the fraction to be separated distills in maximum amounts. Eleven process claims.

- 85b. Hickman, Kenneth C. D. (to Eastman Kodak Co.)
U. S. patent 2,124,879
Application November 21, 1936
Patented July 26, 1938

VACUUM DISTILLATION PROCESS

An improvement of U. S. patent 2,113,302, wherein an indicator is used only on pilot molecular distillations to determine the temperature at which the desired fraction should be collected; thus, the indicator does not have to be used on the bulk of the distilland. Seven process claims.

- 85c. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 479,802
Application March 5, 1937
Convention dates (United States) March 5 and November 21, 1936
Complete specification accepted February 11, 1938

IMPROVEMENTS IN HIGH VACUUM DISTILLATION PROCESSES

Similar to U. S. patent 2,113,302 and 2,124,879. Thirteen process claims.

- 85d. Eastman Kodak Co.
French patent 825,979
Application March 5, 1937
Prior applications in United States March 5 and November 21, 1936
Granted December 27, 1937
Published March 18, 1938

PERFECTIONNEMENTS AUX PROCÉDÉS DE DISTILLATION

Similar to U. S. patents 2,113,302 and 2,124,879. Thirteen process claims.

86. Waterman, Hein I., and van Vlodrop, Cornelus (to Shell Development Co.)
U. S. patent 2,159,303
Application February 26, 1937
In the Netherlands March 5, 1936
Patented May 23, 1939

MULTISTAGE EVAPORATOR

A multistage evaporator, apparently suitable for high-vacuum short-path distillation, is described. The apparatus consists of a series of vertical tubes forming a series of vacuum-tight concentric chambers. By suitable connections to vacuum pumps, a stepwise pressure gradient may be maintained in the series of chambers, the pressure being highest in the outermost chamber and lowest in the innermost chamber. The outermost chamber is surrounded by a heating element, while a cooling element is installed within the innermost tube. The outer surface of a given tube forms the condensing surface for one chamber, while the inner surface of the same tube forms the evaporating surface for the chamber next within. Provision is made to withdraw distillates from the bottom of each chamber, and to pump undistilled residues from the bottom of a given chamber to the top of the distilling surface of the chamber next within. Two claims for apparatus: (Parent Dutch patent not at hand.)

- 7a. Hickman, Kenneth C. D. (to Eastman Kodak Co.)
U. S. patent 2,117,802
Application April 18, 1936
Patented May 17, 1938

DISTILLATION PROCESS

A single molecular still may be used to perform the functions of a multistage still if, instead of circulating distilland over a number of successive columns, the distilland from a single column is collected and continuously recycled over the evaporating surface of the same column. The use of a single unit obviates difficulties of temperature and pressure control inherent in the use of several successive units; further, fewer pumps, evaporating elements, and condensing elements are required.

In addition to the single-column cyclic still, there are described and illustrated a multi-unit still having a plurality of vaporizing surfaces and a common condensing surface; and a still employing a plurality of the single-column cyclic units. Four claims for apparatus and four for the cyclic process.

- b. Eastman Kodak Co. (assignee of Kenneth C. D. Hickman)
British patent 479,816
Application April 19, 1937
Convention date (United States) April 18, 1936
Complete spec. accepted February 11, 1938

IMPROVEMENTS IN DISTILLATION PROCESS

Similar to U. S. patent 2,117,802. Nine process claims.

- 87c. Eastman Kodak Co.
French patent 826,474
Application April 17, 1937
Prior application in United States April 18, 1936
Granted January 4, 1938
Published March 31, 1938

PERFECTIONNEMENTS AUX PROCÉDÉS DE DISTILLATION DANS LE VIDE

Similar to U. S. patent 2,117,802. Fourteen claims.

- 88a. Baxter, James G. (to Distillation Products, Inc.)
U. S. patent 2,169,192
Application June 12, 1936
Patented August 8, 1939

HYDROCARBONS FROM VACUUM DISTILLATION OF FISH OIL

Hydrocarbons are recovered from marine animal oils during the process of molecular distillation thereof. They may be collected in cooled traps placed between still and pumps, or collected together with vitamins, etc., in the early distillate fractions, thereafter being purified by various means. Six claims for hydrocarbons so obtained.

- 88b. Eastman Kodak Co. (assignee of James G. Baxter)
British patent 501,841
Application July 2, 1937
Convention date (United States) June 12, 1936
Complete spec. accepted March 2, 1939

AN IMPROVED PROCESS FOR OBTAINING HYDROCARBONS FROM MARINE ANIMAL OILS

Similar to U. S. patent 2,169,192. Five claims for the process and one for hydrocarbons produced thereby.

- 88c. Eastman Kodak Co.
French patent 823,767
Application June 11, 1937
Prior application in United States June 12, 1936
Granted October 25, 1937
Published January 26, 1938

PROCÉDÉ DE DISTILLATION DANS LE VIDE, EN PARTICULIER D'HUILES D'ANIMAUX MARINS, ET PRODUITS EN RESULTANT

Similar to U. S. patent 2,169,192. Sixteen claims.

89. von Elbe, Guenther J. K., and Scott, Benjamin B., Jr. (to Carnegie Institute of Technology)
U. S. patent 2,198,848
Application June 29, 1936
Patented April 30, 1940

METHOD FOR HIGH VACUUM FRACTIONAL DISTILLATION

Mixtures whose components have different vapor pressures may be fractionally distilled under high vacuum by introducing the mixture into a horizontal sealed container and passing the container longitudinally through a controlled temperature gradient from the cold zone toward the hot zone, at such a speed that the components of the mixture will distill and separate into bands in the container along the gradient. Quantities of distilland as small as 0.001 cm.³ can be successfully handled. The temperature gradient may be above or below room temperature. The separation of mixtures of p- and m-xylene, and of o- and p-nitrotoluene, is described. Seven process claims.

- 90a. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 477,955
Application July 6, 1936
Complete spec. accepted January 6, 1938

IMPROVED METHOD OF FRACTIONAL DISTILLATION

The fractionation obtainable with molecular distillation is improved by an arrangement in which the liquid condensate after moving for some distance in co-current with the distillate vapors is collected and transferred via a conduit protected from the action of the vapors and in a direction counter-current to said vapors before being again exposed to their action. Five claims for process and apparatus.

- 90b. Eastman Kodak Co.
French patent 825,680
Application July 6, 1937
Prior application in Great Britain July 6, 1936
Granted December 16, 1937
Published March 10, 1938

PROCÉDÉ PERFECTIONNÉ DE DISTILLATION ET APPAREIL EN COMPORTANT APPLICATION

Similar to British patent 477,955. Five claims for process and apparatus.

- 91a. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 482,880
Application July 6, 1936
Complete spec. accepted April 6, 1938

METHOD FOR THE PREPARATION OF VITAMIN D IN HIGH YIELDS

Natural vitamin D is composed of a high-boiling ester and a low-boiling form, apparently a sterol resulting from rancidity in the oil or thermal decomposition of the ester. In previous molecular distillation apparatus, vitamin A can be removed from oils in high yields, but the high-boiling form of vitamin D is largely destroyed. In the present apparatus, the distilland is heated for only a short time (flash distillation) in a thin film, preferably after it has been carefully degassed; high yields of vitamin D are thereby obtained.

The cylindrical distilling column is short, but may have as large a diameter as desired. It is divided into segments, each of which can be separately heated to desired temperatures. Between the segments are denticulate bands of wire mesh designed to spread the distilland evenly over the column and to give turbulence to the distilling surface. Apparatus for carefully degassing the oil before distillation is also shown; it includes a centrifugal degassing apparatus comprising a number of superimposed units with an oil seal between each, so that the pressure can be progressively lowered from one unit to the next. Eleven claims for process, apparatus, and composition of matter.

- 91b. Eastman Kodak Co.
French patent 834,532
Application July 6, 1937
-Prior applications in Great Britain July 6, 1936 and the United States
September 5, 1936
Granted August 22, 1938
Published November 23, 1938

PERFECTIONNEMENTS AUX PROCÉDÉS DE DISTILLATION DANS LE VIDE

Similar to British patent 482,880. Six claims for process and apparatus.

- 92a. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 482,881
Application July 6, 1936
Complete spec. accepted April 6, 1938

IMPROVED PROCESS OF VACUUM DISTILLATION

In molecularly distilling minor components from organic substances (e.g., vitamins from oils), the early fractions, being solid or viscous and present in small quantity, often are not easily removable from the still and hence

cannot be cleanly separated. Such fractions can be readily drained and cleanly removed from the still if the distilland is admixed with a synthetic oil compounded to give a constant or known amount of distillate for each increase in temperature. The mixture may be compounded of a number of glycerides, which are blended until the product yields an equal volume of distillate for each equal increment of uniformly increasing temperature. Five claims for process and two for the synthetic mixture.

- 92b. Eastman Kodak Co.
French patent 834,935
Application July 6, 1937
Prior applications in Great Britain July 6, 1936 and the United States
April 1, 1937
Granted September 12, 1938
Published December 6, 1938

PERFECTIONNEMENTS À LA DISTILLATION DANS LE VIDE

Similar to British patent 482,881. Twelve claims for process.

- 93a. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 482,882
Application July 6, 1936
Complete spec. accepted April 6, 1938

IMPROVEMENTS IN VACUUM DISTILLATION

In the high-vacuum distillation of a fluid organic mixture (e.g., a vitamin-containing oil), the mixture is introduced into a chamber onto a whirling disc which produces a fine spray; the spray is heated by a localized body of hot vapors produced by previously introducing into the chamber, in finely divided form, a liquid which has a lower vapor pressure than the material to be distilled, and which is heated on the hot walls of the chamber. The more volatile portions of the distilland are vaporized by this localized body of hot vapors and pass out of a conduit at the top of the chamber to be condensed and removed. Undistilled residue is removed at the bottom of the chamber together with condensate from the body of hot vapors. To avoid contamination of the distillate with vapors from the heating medium, the path of the distillate molecules is usually much longer than their mean free path. Eleven claims for process and one for apparatus.

- 93b. Hickman, Kenneth C. D. (to Eastman Kodak Co.)
U. S. patent 2,117,803
Application December 4, 1936
In Great Britain July 6, 1936
Patented May 17, 1938

VACUUM DISTILLATION PROCESS

Similar to British patent 482,882. Seven process claims.

- 83c. Eastman Kodak Co.
French patent 834,936
Application July 6, 1937
Prior applications in Great Britain July 6, 1936 and the United States
December 4, 1936
Granted September 12, 1938
Published December 6, 1938

PROCEDE DE DISTILLATION DANS LE VIDE

Similar to British patent 482,882. Eleven claims for process and one for apparatus.

- 94a. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 482,833
Application July 6, 1936
Complete spec. accepted April 6, 1938

IMPROVED METHOD OF DISTILLING LARGE QUANTITIES OF LIQUID

The invention aims to carry out molecular distillation at commercial speeds without formation of thick films of distilland. Thin films are formed on the distilling surface either by centrifugal means or by pressure rollers bearing against a horizontal rotating distilling surface. New apparatus is described. Seven claims for process and two for apparatus. (See also British patent 500,195, Abstract 115a).

- 94b. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,180,050
Original application September 5, 1936
Divided and this application October 1, 1937
Patented November 14, 1939

VACUUM DISTILLATION APPARATUS

Corresponds to that part of British patent 482,883 which deals with an apparatus having a revolving internally-heated drum for a distilling surface, and an outer concentric cooled stationary drum for a condensing surface. The distilland is spread by rollers in a thin film on the surface of the revolving drum; distillate is removed by troughs on the condensing surface. Two claims for apparatus.

- 94c. Eastman Kodak Co.
French patent 834,937
Application July 6, 1937
Prior applications in Great Britain July 6, 1936 and the United States
September 5, 1936
Granted September 12, 1938
Published December 6, 1938

PERFECTIONNEMENTS AUX PROCÉDÉS DE DISTILLATION SOUS VIDE POUSSÉ

Similar to British patent 482,883. Seven claims for process and one for apparatus.

95. Gurin, Samuel
J. Am. Chem. Soc. 58, 2104 (1936)
Received for publication August 10, 1936; issue of November 1936

HIGH VACUUM DISTILLATION OF N-ACYL AMINO ACID AND POLYPEPTIDE ESTERS

Butyl esters of benzenesulfonylated amino acids can be distilled without decomposition or racemization at pressures of 10^{-6} to 10^{-7} mm. with the air of a mercury vapor pump of the Phipps type. The molecular still used is not described.

- 96a. Fawcett, Eric W., Burrows, Godfrey, and Imperial Chemical Industries, Ltd.
British patent 480,265
Application August 19, 1936
Complete spec. accepted February 21, 1938

IMPROVEMENTS IN OR RELATING TO HIGH-VACUUM DISTILLATION AND APPARATUS THEREFOR

In a molecular still of the vertical surface type, means such as bands or spirals of metal gauze, are provided on the evaporating surface for temporarily checking or disturbing the flow of distilland and mixing it so as to expose a fresh outer surface from time to time. Also, the distilling surface may be provided with combinations of recesses and baffles for making the oil turbulent. Five claims for apparatus.

- 96b. Fawcett, Eric W., and Burrows, Godfrey (to Imperial Chemical Industries, Ltd.)
U. S. patent 2,186,669
Application August 7, 1937
In Great Britain August 19, 1936
Patented January 9, 1940

APPARATUS FOR HIGH-VACUUM DISTILLATION

Similar to British patent 480,265. Two claims for apparatus.

- 6c. Imperial Chemical Industries, Ltd.
French patent 825,773
Application August 19, 1937
Prior application in Great Britain August 19, 1936
Granted December 16, 1937
Published March 14, 1938

PERFECTIONNEMENTS À LA DISTILLATION SOUS UN VIDE POUSSÉ, ET APPAREIL
APPROPRIÉ

Similar to British patent 480,265. Four claims for apparatus.

97. Mair, Beveridge J., and Schicktanz, Sylvester T.
J. Res. Nat. Bur. Standards 17, 909 (1936) (Research Paper RP 953)
Dated September 2, 1936; issue December 1936

EXTRACTION, WITH ACETONE, OF SUBSTANTIALLY CONSTANT-BOILING FRACTIONS OF
A "WATER-WHITE" LUBRICATING OIL

The column and pot-type molecular stills previously described (Abstract 71)
were used in continued experiments on the fractionation of petroleum
constituents.

- 8a. Smith, Gerald G. R. (to Distillation Products, Inc)
U. S. patent 2,207,385
Application September 21, 1936
Patented July 9, 1940

PREPARATION OF VITAMIN CONCENTRATE

Mixtures of vitamins A and D in their high-boiling (ester) form are
difficult to fractionate because of the similar evaporating ranges of the
two esters. Separation of molecular distillates containing such mixtures
is accomplished by saponifying the esters, adding a suitable solvent (e.g.,
a fish oil) to the unsaponifiable, and redistilling the vitamins in their
low-boiling (free alcohol) form. Six process claims.

- 8b. Eastman Kodak Co. (assignee of Gerald G. R. Smith)
British patent 487,367
Application September 17, 1937
Convention date (United States) September 21, 1936
Complete spec. accepted June 20, 1938

PREPARATION OF VITAMIN CONCENTRATE

Similar to U. S. patent 2,207,385. Seven process claims.

- 99a. Fawcett, Eric, W., Myles, James R., and Imperial Chemical Industries, Ltd.
British patent 487,771
Application September 22, 1936
Complete spec. accepted June 22, 1938

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF STIGMASTEROL

Stigmasterol concentrates may be obtained by molecular distillation of soybean, calabar bean, and other oils. The distillate may be redistilled and stigmasterol isolated by known methods. Six claims.

- 99b. Imperial Chemical Industries, Ltd.
French patent 830,023
Application September 22, 1937
Prior application in Great Britain September 22, 1936
Granted May 2, 1938
Published July 19, 1938

PROCEDE DE FABRICATION DU STIGMASTEROL

Similar to British patent 487,771. Five claims.

100. Hickman, K.
Nature 138, 881 (1936)
Dated October 9, 1936; issue of November 21, 1936

IDENTIFICATION OF VITAMINS BY MOLECULAR DISTILLATION

"When oils containing vitamins are submitted to molecular distillation (Abstracts 11, 14, 20, 37a), the fractions removed as the temperature rises contain successively more vitamin until a maximum is reached, after which the potency falls rapidly to zero because all the vitamin has been eliminated. The elimination follows a simple law and the ideal elimination curve possesses a slightly skew shape which is easily recognizable. Deviations from the shape indicate imperfect conditions of distillation or the presence of more than one form of the vitamin. The maximum of the curve can be located with an accuracy of $\pm 2^{\circ}\text{C}.$, and is as definite a characteristic as a boiling point, if less precise. Separate elimination curves can be detected for more than one material if the maxima are $5^{\circ}\text{C}.$ apart. When two potent materials yield different maxima, it is proof that they are different substances. Coincident maxima provide only partial evidence that the substances are identical. When oils containing traces of many impurities are distilled, their maxima occur in a fixed order, and if one can be identified, the others may be recognized. This enables dyes, etc., to serve as distillation pilots."

"Elimination curves can be found more accurately if the distillation is made from an oil which yields a constant quantity of distillate for each equal increment of the absolute temperature. Such an oil can be made by

esterifying glycerin with a mixture of fatty acids. By mixing various fish oils with this constant yield oil, it has been found that the vitamin A in the cod liver and halibut liver oils exists almost entirely in the form of esters. The distortion of the curve shows that the esters are derived from most of the fatty acids present. A very small quantity of vitamin A alcohol is also found. . . The vitamin D in cod liver oil yields a maximum halfway between the vitamin A alcohol and esters. . . Evidently vitamin D occurs partly free and partly as a mixture of esters, the esters surviving for only a few seconds at the temperature of distillation. . . "

101. Dam, Henrik, and Schönheyder, Fritz
Nord. med. Tidsskr. 12, 1097 (1936)

(SUBLIMATION OF VITAMIN K IN HIGH VACUUM)

It is stated by Dam and Lewis (102); "As already mentioned by Dam and Schönheyder, vitamin K can be sublimed in a high vacuum."

102. Dam, Henrik, and Lewis, Liese
Biochem. J. 31, 17 (1937)
Received for publication November 12, 1936

THE CHEMICAL CONCENTRATION OF VITAMIN K

A vitamin K concentrate was distilled in a molecular still of the type described by Breusch (Abstract 57), but with a ground joint instead of a rubber stopper to connect the condensing tube to the outer jacket. The pump was of the Gaede mercury diffusion type, and the pressure was controlled by a Gaede mol-vacuummeter. All connections were of glass; apiezon grease was used to lubricate ground joints. During a 3-hour run with 54 mg. of concentrate at a pressure of 0.6×10^{-3} mm., three fractions were collected (130-155°, 155-200°, and 200-250°). Of these the first fraction (20 percent) had a potency of 700,000 units per gram, as compared with a potency of 200,000 units per gram for the original distilland. In a second experiment with 621 mg. of concentrate at a pressure of 2×10^{-3} mm, the most potent fraction (10 percent) was removed between 160 and 180°. Distillation at 0.1 mm. and up to 250° led to destruction of the greater part of the vitamin.

- 103a. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,180,356
Application November 27, 1936
Patented November 21, 1939

VACUUM DISTILLATION OF OILS CONTAINING VITAMINS

A continuation in part of previous patents. The invention claims "in the process of molecular distillation of fish oils to obtain concentrated fat soluble vitamins the steps which comprise segregating components distilling up to 170°C., separating a fraction at between about 170° and 195°C. and returning it to the fresh incoming oil to be distilled, and separating a fraction high in vitamin content at a temperature between about 195° and 230°C."

103b. Kodak, Ltd. (assignee of Kenneth C. D. Rickman)

British patent 508,469

Application November 27, 1937

Convention date (United States) November 27, 1936

Complete spec. accepted June 27, 1939

IMPROVEMENTS IN VACUUM DISTILLATION OF OILS CONTAINING FAT SOLUBLE VITAMINS

Similar to U. S. patent 2,180,356. Five claims relating to the removal of vitamins from oils in general.

103c. Eastman Kodak Co.

French patent 834,540

Application November 27, 1937

Prior application in United States November 27, 1936

Granted August 22, 1938

Published November 23, 1938

PERFECTIONNEMENTS À LA DISTILLATION DANS LE VIDE D'HUILES CONTENANT DES VITAMINES

Similar to U. S. patent 2,180,356. Fourteen process claims.

104a. Kodak, Ltd. (Assignee of Eastman Kodak Co.)

British patent 484,736

Application December 24, 1936

Complete spec. accepted May 10, 1938

IMPROVEMENTS IN THE PURIFICATION OF SOYA BEAN OIL

Molecular distillation of crude soybean oil is difficult because decomposition of phosphatides and similar impurities leads to the evolution of considerable quantities of gas; low pressures cannot be maintained, and yields are low and of poor quality. The difficulty can be avoided by removal of phosphatides prior to distillation. For example, 2 volumes of acetone and .005 volume of saturated alcoholic solution of magnesium chloride are added to 1 volume of soybean oil; precipitated phosphatides are filtered off, and acetone is removed in a solvent recovery still.

The purified oil, on molecular distillation, gives glyceride fractions which are odorless, edible, and do not develop a "grassy" taste or odor on exposure to atmosphere, even over long periods of time. Seven claims for process and soybean oil prepared thereby.

- 104b. Tischer, Arthur O. (to Eastman Kodak Co.)
U. S. patent 2,117,776
Application March 5, 1937
In Great Britain December 24, 1936
Patented May 17, 1938

PURIFICATION OF SOY BEAN OIL

Similar to British patent 484,736. Sixteen claims for process.

- 104c. Eastman Kodak Co.
French patent 831,255
Application December 24, 1937
Prior applications in Great Britain December 24, 1936 and the
United States March 5, 1937
Granted May 30, 1938
Published August 29, 1938

PERFECTIONNEMENTS AUX PROCÉDÉS DE PURIFICATION DE L'HUILE DE FÈVES DE SOYA

Similar to British patent 484,736. Six claims for process.

105. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 493,948
Application April 20, 1937
Complete spec. accepted October 18, 1938

IMPROVED METHOD OF HIGH VACUUM DISTILLATION

In order to achieve fractionation during the molecular distillation of minor components from an organic mixture, a carrier liquid is added to the distilland. One of the carrier liquid fractions distills contemporaneously with each of the desired minor components, and is afterward removed therefrom. For example, in distilling a substance containing cholestane and stigmaterol, a carrier liquid consisting of tripalmitin and tricaproin is added to the distilland. The cholestane distills at substantially the same temperature as the tricaproin, while the stigmaterol distills with the tripalmitin. The glycerides are removed from the distillates by saponification. Five process claims.

106. Killeffer, D. H.
Ind. Eng. Chem. 29, 966 (1937)
Issue of September 1937

MOLECULAR DISTILLATION. USEFUL FACILITY

An informal review of the principles of molecular distillation and its history from the standpoint of commercial applications.

107. Hickman, K. C. D.
Ind. Eng. Chem. 29, 968 (1937)
"Received for publication June 1, 1937; issue of September 1937

MOLECULAR DISTILLATION. APPARATUS AND METHODS

The advantages of column molecular stills, as compared with pot-type stills, are discussed. A cyclic column still is described and illustrated. The evaporator is a polished metal tube 15 cm. long and 3.7 cm. in diameter, heated internally by a resistance coil submerged in oil. Two wire mesh collars are fastened around the top of the column to aid in spreading the distilland over its surface; in addition, the column may be spirally embossed. The evaporator is surrounded by a glass air-cooled condenser tube, at the bottom of which is an annular trough connected to a flask for collecting distillates. Below the column are two reservoirs and a nickel-glass circulating pump operated by an electromagnet.

Oil is circulated from the lower reservoir through the pump and up a pre-heating tube to the top of the evaporator. Undistilled residue flows through a cooler to the upper of the two reservoirs, which may be closed off from the lower reservoir by means of a magnet-operated steel ball; by means of this valve recirculation of oil can be made continuous or periodic, as desired. Another ball valve in the distillate drainage tube permits changing receivers at atmospheric pressure.

For ready demountability the still units are assembled with rubber stoppers or gaskets; high vacua are maintained by use of a condensation pump of large capacity (10-20 l. per sec.). Pressures are measured with a Pirani gauge.

The use of the still in concentrating minor constituents (e.g., vitamins) of oils is discussed; and the application of elimination curves in identifying such constituents is described in detail.

108. Embree, N. D.
Ind. Eng. Chem. 29, 975 (1937)
Received for publication June 1, 1937; issue of September 1937

MOLECULAR DISTILLATION. THEORY OF ELIMINATION CURVE

Hickman (preceding abstract) has shown that certain substances which distill under molecular conditions may be studied and identified by means of elimination curves. In the present paper such curves are derived by theoretical methods. The effect of the properties of the substances distilled and the effect of the nature of the distillation procedure upon the shape and location of these curves are indicated by several examples.

109. Hickman, K. C. D.
Ind. Eng. Chem. 29, 1107 (1937)
Received for publication June 1, 1937; issue of October 1937

MOLECULAR DISTILLATION. STATE OF THE VITAMINS IN CERTAIN FISH-LIVER OILS

Distillation of fish oils in a molecular still gave a vitamin-rich fraction evaporating below 190° and a mixture of glycerides evaporating at 190-250°. The free vitamins were largely contained in the first 3 percent of the distillate. Constant-yield oil was added to increase this fraction to 25 percent and to allow elimination curves to be determined. Two elimination curves for vitamin A were found with maxima at 125° and 220°, probably corresponding to the free vitamin and to a mixture of its esters, one of which is the palmitate. Vitamin D likewise showed maxima for the free vitamin (162°) and its esters (230-250°). An economical method of biological assay using a stepped one-rat system is described. (Chemical Abstracts 31:8259).

110. Baxter, J. G., Gray, E. Leb., and Tischer, A. O.
Ind. Eng. Chem. 29, 1112 (1937)
Received for publication June 1, 1937; issue of October 1937

MOLECULAR DISTILLATION. PREPARATION AND CHARACTERISTICS OF SYNTHETIC CONSTANT-YIELD MIXTURES

In applying the method of elimination curves to a study of vitamins molecularly distilled from fish-liver oils, it is desirable to mix vitamin concentrates with a synthetic oil which distills over the range 100-260°C., yielding approximately the same weight of distillate for each equal increment of temperature. A constant-yield oil was prepared by esterifying with glycerol a blend of acetic and butyric acids, the mixture of myristic and lauric acids from saponified coconut oil, and the unsaturated C₁₈ acids from saponified perilla oil. This oil gave fairly constant yields over the range 100° to 220°C; the range was extended to 260° by addition of cod-liver oil from which unsaponifiables had been removed.

- 111a. Fawcett, Eric W., and Imperial Chemical Industries, Ltd.
British patent 501,194
Application June 18, 1937
Complete spec. accepted February 20, 1939

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION AND UTILISATION OF ANTIOXIDANTS

Fats and oils containing natural antioxidants are molecularly distilled to obtain relatively small early fractions containing the bulk of the volatile antioxidants. Such concentrates can be used to stabilize vegetable, animal and fish oils and fats, or other materials readily susceptible to atmospheric oxidation.

- 111b. Imperial Chemical Industries, Ltd.
Belgian patent 428,704

Apparently similar to British patent 501,194. Patent not at hand.

- 111c. Imperial Chemical Industries, Ltd.
French patent 839,496
Application June 18, 1938
Prior application in Great Britain June 18, 1937
Granted January 4, 1939
Published April 4, 1939

PROCÉDE DE DISTILLATION SOUS VIDE ÉLEVÉ DES GRAISSES ET HUILES GRASSES

Similar to British patent 501,194. Nine claims.

112. Almquist, H. J.
J. Biol. Chem. 115, 589 (1936)
Received for publication June 24, 1936; issue of September 1936

PURIFICATION OF THE ANTIHEMORRHAGIC VITAMIN BY DISTILLATION

A concentrate of the antihemorrhagic vitamin prepared from alfalfa meal was fractionated in a pot-type molecular still. The fraction removed at 120-45° (38 percent), a yellow viscous oil, proved to be at least four times as potent as the original concentrate.

The still comprises an outer glass cylinder in which is mounted an upright water-cooled condensing tube whose flattened bottom is 3.5 cm. from the bottom of the jacket. Heat is supplied by an electrically-heated oil bath. A pressure of about 10^{-6} mm. is maintained by use of two glass oil-vapor diffusion pumps.

113. Almquist, H. J.

J. Biol. Chem. 120, 635 (1937)

Received for publication June 26, 1937; issue of September 1927

FURTHER STUDIES ON THE ANTIHEMORRHAGIC VITAMIN

By further improvements in the purification of vitamin K it has been obtained in a crystalline fraction. A new type of molecular still was employed for the distillation of a concentrate from commercially dehydrated alfalfa. It consists of a horizontal glass tube 2.5 cm. in diameter and 40 cm. long; one end is sealed and rounded, while the other is fitted with a ground joint. Two circular constrictions divide the apparatus into three compartments, A at the closed end, B in the middle, and C at the end with the joint. Distilland is placed in compartment A, which is electrically heated to 160°; compartment B is heated to 65°. Pressure is maintained at 10^{-5} mm. or less. During the distillation the tube is rotated to present new surfaces for evaporation.

The vitamin B, as well as a quantity of sterols, is collected in the middle compartment B as an orange, oily fraction volatile at 160° but not at 65°. The 65° distillate in compartment C contains no detectable quantity of the vitamin. The vitamin fraction from B can be further purified by redistillation with a temperature of about 130° in compartment A.

114. Bömer, A., and Hüttig, H.

Z. Unters. Lebensmittel 75, 1 (1938)

Received for publication July 19, 1937; issue of January 1938

BEITRÄGE ZUR KENNENIS DER GLYCERIDE DER FETTE. XV. GLYCERIDE DES BARASSUFETTES

Glycerides of babassu oil were separated by distillation in a 100-cc Anschütz distillation flask having a sausage side-arm and connected to a Krafft falling mercury pump whereby high-vacuum non-ebullient distillation was effected. It is doubtful that an uninterrupted path obtained between distilling and condensing surfaces. The bulk of the glycerides distilled between 261 and 282°.

115a. Kodak, Ltd. (assignee of Eastman Kodak Co.)

British patent 500,195

Application July 29, 1937

Patent of addition to British 482,883, dated July 6, 1936

Complete spec. accepted January 30, 1939

IMPROVEMENTS IN AND RELATING TO HIGH VACUUM DISTILLATION

An improvement to that portion of British 482,883 (Abstract 94a) describing centrifugal molecular stills in which the distilland is fed to a rotary surface over which it passes in a thin film to be thrown off at the edge as a spray and collected in a concentric gutter separate from the rotary surface.

In the present invention the external gutter is dispensed with, and the liquid is collected from the edge on the rotary distilling or condensing surface by means of a pen, scoop, tube, or wiper. Nine claims for process and apparatus.

- 115b. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,180,053
Application June 29, 1938
In Great Britain July 29, 1937
Patented November 14, 1939

DISTILLATION APPARATUS

Similar to British patent 500,195. Eight claims for apparatus.

- 115c. Eastman Kodak Co.
French patent 49,278
Application October 25, 1937
Prior applications in Great Britain October 23, 1936 and July 29, 1937
Granted November 12, 1938
Published February 16, 1939

PERFECTIONNEMENTS AUX PROCÉDÉS DE DISTILLATION SOUS VIDE POUSSÉ

Addition to French patent 834,937. Corresponds in general with British patent 500,195. Eight claims.

116. Jenaer Glaswerke Schott u. Gen., Jena
Circular No. 5917, July 1937; Circular No. 6268, June 1938

Various applications of molecular distillation are enumerated.

117. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 507,471
Application September 10, 1937
Complete spec. accepted June 12, 1939

IMPROVEMENTS IN TREATING ANIMAL AND VEGETABLE OILS AND FATS FOR RETARDING OXIDATION AND THE DEVELOPMENT OF RANCIDITY

Oxidation and the development of rancidity in animal and vegetable oils and fats are retarded by addition of a small quantity of a fraction possessing antioxidant properties, taken from the first 20 percent of distillate obtained by molecular distillation of vegetable oils and raw materials from which such vegetable oils are derived. Four claims.

118. Emerson, Oliver H., Emerson, Gladys A., Mohammad, Ali, and Evans, Herbert M.
J. Biol. Chem. 122, 99 (1937)

Received for publication October 7, 1937

THE CHEMISTRY OF VITAMIN E. TOCOPHEROLS FROM VARIOUS SOURCES

By molecular distillation of unsaponifiable matter from palm oil a concentrate was obtained having an absorption maximum at 298 m μ . and definite vitamin E activity. An α -tocopherol allophanate (m. 158-60°) was obtained therefrom. The glass pot still, of the Washburn type, contains a condenser tube 3.5 cm. in diameter, which is cooled with dry ice or liquid air. Attached to the condenser by means of a No. 50 ground joint is the outer jacket, 5 cm. in diameter, having a flattened bulb at the bottom.

- 119a. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,199,994

Application November 13, 1937

Patented May 7, 1940

VACUUM DISTILLATION

In order to obtain high distillation rates and reduced heat losses, the vaporizing surface of the still is heated to a temperature higher than that required for true molecular distillation, and sufficient to yield a vapor stream of distillate having a density such that the molecules travel more than five times their mean free path in passing to the condensing surface.

- 119b. Eastman Kodak Co.

French patent 845,957

Application November 14, 1936

Prior application in United States November 13, 1937

Granted May 22, 1939

Published September 6, 1939

PROCÉDE DE DISTILLATION DANS LE VIDE

Similar to U. S. patent 2,199,994. Seven claims.

120. Farmer, Ernest H., and van den Heuvel, Frantz Aime'
J. Soc. Chem. Ind. 57, 24T (1938)

Received for publication November 16, 1937; issue of January 1938

SEPARATION OF THE HIGHLY-UNSATURATED ACIDS OF FISH OILS BY MOLECULAR DISTILLATION

Attempts to separate the unsaturated acids of fish oils (codliver, halibut liver, and Japanese sardine) by ordinary vacuum distillation resulted in isomerization and polymerization. Very satisfactory results were obtained

by use of a column molecular still, in which thoroughly degassed methyl esters were allowed to flow in a uniform thin film over the surface of a heated vertical glass cylinder. A coaxial outer glass cylinder formed the condensing surface. The chamber was evacuated to about 10^{-4} mm. Distillate was removed through a tube in the bottom of the heating surface into a funnel leading through the bottom of the still to a second receiver.

Distillation at temperatures between 56° and 95° resulted in a series of fractions which were homogeneous as regards the chain-length of the component acids (C_{16} , C_{18} , C_{20} , and C_{22}). The principal (C_{22}) fraction was also homogeneous as regards degree of unsaturation, although not necessarily so as to position of double bonds; it was shown to be a hexaene acid and not a pentaene (clupanodonic) acid, as previously reported by others. The C_{16} , C_{18} , and C_{20} fractions were all mixtures of two or more acids of different degrees of unsaturation.

The fractionation of mixtures under molecular conditions is treated mathematically, and the effect of concentration, vapor pressure, molecular weight, mean free path, etc., are discussed in detail. Because of similarity in vapor pressure, it is impossible to separate by distillation acids with the same chain length, but differing in degree of unsaturation, unless one of the acids is present in high concentration. In general, the degree of separation of two substances will be better the lower the temperature.

A linear relationship obtains between n_D (or n_D') values and refractive indices, thereby it can be determined whether a fraction was an original component of an oil or only a heat-altered one.

121. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,180,051
Application December 1, 1937
Patented November 14, 1939

REMOVAL OF GAS FROM ORGANIC LIQUIDS

Prior to the high-vacuum distillation of vitamin-containing fish oils, absorbed gases and oxidizing agents are substantially completely removed by subjecting the oil in the form of a thin film to extreme agitation and to a pressure less than about .005 mm., and maintaining the agitation and reduced pressure until the internal pressure of the gas in the oil is below about .015 mm. Two claims for process.

122. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,197,539
Application December 1, 1937
Patented April 16, 1940

DEGASSING APPARATUS

Apparatus for degassing organic liquids prior to high-vacuum distillation is described. It consists of a vertical cylindrical casing divided by partitions into a series of chambers. Each chamber can be separately evacuated and contains a horizontal disc fixed to a central vertical shaft which can be rotated. Oil seals between chambers permit progressive lowering of the pressure in successive chambers from top to bottom. Oil admitted to the uppermost chamber is thrown off the rotating disc by centrifugal action, flows down the casing wall and the conical partition and through the oil seal, and is admitted to the center of the disc in the chamber next below. One claim for apparatus.

- 123a. Baxter, James G., and Edwards, Robert L. (to Distillation Products, Inc.)
U. S. patent 2,197,546
Application December 1, 1937
Patented April 16, 1940

PURIFICATION OF ESTERS

Diesters of phthalic acid, suitable for use in condensation pumps, are purified by refluxing the ester with a salt of perboric acid under reduced pressure, separating the ester from the salt and subjecting it to vacuum distillation. Eleven claims for process.

- 123b. Kodak, Ltd. (assignee of Eastman Kodak Co.)
British patent 511,070
Application February 14, 1938
Complete spec. accepted August 14, 1939

PURIFICATION OF ESTERS OF LOW VAPOR PRESSURE

Similar to U. S. patent 2,197,546. Eight claims for process and esters purified thereby.

124. Gillam, A. E., Heilbron, I. M., Jones, W. E., and Lederer, E.
Biochem. J. 32, 405 (1938)
Received for publication December 31, 1937

ON THE OCCURRENCE AND CONSTITUTION OF THE 693 m μ . CHROMOGEN (VITAMIN A₂?) OF FISH LIVER OILS

Attempts were made to separate the 693 m μ . chromogen from vitamin A by vacuum distillation and chromatographic adsorption, without success. The distillation apparatus is not described, but according to Embree (J. Biol. Chem. 132, 619 (1940)) it was of the molecular still type.

- 125a. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,218,240
Application January 28, 1938
Patented October 15, 1940

VACUUM DISTILLATION

The apparatus contains, within an evacuated chamber, a series of pairs of closely adjacent horizontal discs mounted on a vertical rotatable axis. One disc of each pair serves as the evaporating surface, the other as the condensing surface. Means are provided for conveying condensate onto the evaporating surfaces in succession, and for conveying undistilled residue onto the evaporating surfaces on reverse succession. The apparatus is suitable for distillation of hydrocarbons and of animal and vegetable oils (e.g., linseed, soybean, or cod-liver oils) to recover unsaturated glycerides, sterols, or vitamin concentrates. Five claims.

- 125b. Eastman Kodak Co. (assignee of K. C. D. Hickman).
British patent 524,390
Application January 28, 1939
Convention date (United States) January 28, 1938
Complete spec. accepted August 6, 1940

IMPROVEMENTS IN VACUUM DISTILLATION

Within an evacuated still chamber a number of superimposed evaporating and condensing discs, alternately spaced, are attached to a vertical rotatable shaft. Means are provided for conveying condensate from a condensing surface to the next heating surface in succession, the undistilled residue from a heating surface being pumped to a preceding heating surface. This countercurrent recycling of distillates and residues is claimed to promote more efficient fractionation of mixtures. Eight claims for process and apparatus.

- 125c. Eastman Kodak Co. (assignee of K. C. D. Hickman)
British patent 524,439
Application January 28, 1939
Convention date (United States) January 28, 1938
Complete spec. accepted August 6, 1940

IMPROVEMENTS IN VACUUM DISTILLATION

A cylindrical column molecular still is divided into several superimposed zones which increase in area from top to bottom. The evaporating surface of each zone may be heated independently, while a separate annular collecting trough is provided for each zone of the condensing surface. To provide more efficient fractionation of mixtures, the condensate from a given condensing surface is collected and pumped to a succeeding heating surface, while the residue from any heating surface is pumped back to a preceding heating surface. Eight claims for apparatus and process.

126. Farmer, Ernest H., and van den Heuvel, Frantz Aime'
J. Chem. Soc. 1938, 427

Received for publication February 8, 1938

UNSATURATED ACIDS OF NATURAL OILS. VII. DOCOSAHEXAENOIC ACID, AN ABUNDANT
HIGHLY-UNSATURATED ACID OF COD-LIVER OIL

The unsaturated acids from cod-liver oil were subjected to distillation (as methyl esters) in the column molecular still previously described (Abstract 120), at pressures around 10^{-4} mm. and temperatures up to 110°C . The most abundant (C_{22}) fraction appeared to be homogeneous as regards degree of unsaturation; displaying hexaene unsaturation and yielding pure behenic acid on complete hydrogenation, it is regarded as docosaheptaenoic acid, $\text{C}_{22}\text{H}_{22}\text{O}_2$.

127. Hickman, Kenneth C. D., and Hecker, John C. (to Distillation Products, Inc.)
U. S. patent 2,180,052

Application March 9, 1938

Patented November 14, 1939

VACUUM DISTILLATION APPARATUS

New modifications of gravity flow and centrifugal high-vacuum stills are described. Thirteen claims for apparatus.

128. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,199,995

Application March 15, 1938

Patented May 7, 1940

PREPARATION OF VITAMIN COMPOSITIONS

Vitamin concentrates are obtained from oils (e.g., pollack-liver oil) by a process which involves neutralizing the free fatty acids (suitably with aqueous sodium hydroxide) without causing substantial saponification of the oil, separating the soaps from the oil, and subjecting the latter to high-vacuum distillation. Six claims.

129. Hickman, K. C. D., and Gray, E. LoB.
Ind. Eng. Chem. 30, 796 (1938)

Received for publication March 24, 1938; issue of July 1938

MOLECULAR DISTILLATION. EXAMINATION OF NATURAL VITAMIN D

Examination by molecular distillation and rat assay of the fractions of calciferol shows that it has a simple elimination curve. Cod-liver oil has a complex curve indicating two chief vitamins D, two present in lesser

quantities and traces of two more. The curves for spearrish and white sea bass are different from each other and from cod-liver vitamin D. The lowest-boiling vitamin D is probably devoid of side chains on the C₁₇ atom of the cholane nucleus.

130. Knight, Henry G.
Ind. Eng. Chem., News Ed. 16, 291 (1938)
Issue of May 20, 1938

INDUSTRIAL ACCOMPLISHMENTS AT THE NEW SOYBEAN LABORATORY

Progress is reported in the use of molecular distillation at the U. S. Regional Soybean Industrial Products Laboratory, in studies of the composition and characteristics of soybean oil.

131. Tischer, A. O.
J. Biol. Chem. 125, 475 (1938)
Received for publication June 29, 1938; issue of October 1938

THE NATURE OF VITAMIN A IN COD-LIVER OIL

From a cod-liver oil concentrate obtained by molecular distillation a vitamin A ester was isolated in the form of its dimaleic anhydride addition compound and was identified as vitamin A palmitate. It is present in the oil to the extent of approximately 3 percent of the total esters.

132. Bills, C. E., Massengale, O. N., Hickman, K. C. D., and Gray, E. LeB.
J. Biol. Chem. 126, 241 (1938)
Received for publication July 12, 1938; issue of November 1938

A NEW VITAMIN D IN COD-LIVER OIL

Bio-assays were carried out on the most volatile vitamin D fraction of cod-liver oil, which had been separated by molecular distillation from commercial Norwegian cod-liver oil. The assays substantiated the evidence previously obtained from molecular distillation, that cod-liver oil contains several vitamins D.

133. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,221,691
Application September 28, 1938
Patented November 12, 1940

VACUUM DISTILLATION

A commercial-scale falling film still is described, in which the condensing surface, surrounding and coaxial with the evaporating surface, is located at a distance from the latter greater than three times the mean free path of the distilling molecules. The vapor pressure of the distilling molecules is maintained at a pressure between 10^{-3} and 10^{-7} mm. Three claims.

134. Almquist, H. J.
Proc. Seventh World's Poultry Congr. and Expos. (Cleveland), 1939, 138
Written in September 1938

PROPERTIES OF VITAMIN K

Vitamin K can be purified by distillation in a molecular still at temperatures between 120° and 160°C .

135. Fawcett, E. W.
Kolloid-Z. 86, 34 (1939)
Received for publication September 1938; presented at Symposium on Chemistry and Pharmacy, Jena, October 3 and 4, 1938

MOLEKULAR-DISTILLATION

A comprehensive review of the theory, technique, and applications of molecular distillation. Several designs of pot-type and column molecular stills are described and illustrated.

136. Burch, C. R., and van Dijck, W. J. D.
J. Soc. Chem. Ind. 58, 39 (1939)
Lecture presented November 7, 1938; issue of February 1939

THE THEORY AND DEVELOPMENT OF HIGH-VACUUM DISTILLATION

Molecular distillation is characterized by the use of permanent gas pressures so low (10^{-6} atm.) as to play no essential part in determining the speed of distillation, or even whether distillation takes place or not. The historical development of this method of distillation, and the theoretical considerations governing the process, are outlined, and factors limiting the large-scale application are discussed.

Two types of "self-pumping still", which remove the limit set by the finite rate of gas flow in the still itself, are described. The limit set by splashing due to traces of decomposition remains.

137. Fawcett, E. W. M.
J. Soc. Chem. Ind. 58, 43 (1939)
Lecture presented November 7, 1938; issue of February 1939

THE GENERAL TECHNIQUE OF MOLECULAR DISTILLATION. I. THE CHARACTERISTICS AND SCOPE OF THE PROCESS

The general characteristics of the molecular distillation process are discussed and the effect of variables such as pressure, temperature, and gap between evaporating and condensing surfaces on the performance of molecular stills is considered. The main disadvantages of the process are pointed out, namely, limited fractionating power and low thermal efficiency. The general scope of the process is illustrated by consideration of its application to the processing of natural triglyceride oils. It is concluded that the process is unlikely to compete with normal distillation processes in fields where the latter process is applicable and that the molecular distillation process finds its main outlet in the preliminary concentration of materials of a low order of thermal stability.

138. Furrows, Godfrey
J. Soc. Chem. Ind. 58, 50 (1939)
Lecture presented November 7, 1938; issue of February 1939

THE GENERAL TECHNIQUE OF MOLECULAR DISTILLATION. II. GENERAL DESIGN OF MOLECULAR DISTILLATION EQUIPMENT

The technique of molecular distillation demands equipment specially designed to meet the particular requirements of the process, one important feature being the production and maintenance of the high vacuum necessary. In order to make the apparatus proof against the leakage inwards of external air, special precautions have to be observed during the manufacture of the apparatus. The designs of the various joints used must incorporate suitable seals. This paper describes various forms of continuous and discontinuous high-vacuum stills, together with the more important items of equipment. Methods of maintaining the high degree of vacuum required are discussed, and different types of condensation pumps are illustrated and described. The molecular distillation process lends itself conveniently to automatic operation. Various devices available for protection of the plant under conditions of automatic operation are considered.

139. Jewell, W., Mead, T. H., and Phipps, J. W.
J. Soc. Chem. Ind. 58, 56 (1939)
Lecture presented November 7, 1938; issue of February 1939

THE APPLICATION OF MOLECULAR DISTILLATION TO THE CONCENTRATION OF VITAMINS

This paper traces the development of molecular distillation as applied to vitamin A and gives some account of the features of the process which apply more particularly to the treatment of this vitamin. Vitamin A occurs in fish-liver oils, chiefly in the form of fatty acid esters. When concentrated by saponification, free vitamin A alcohol is produced. Molecular distillation has been employed successfully for the concentration and purification of vitamin A on the commercial scale since 1932. The concentration of vitamin A directly from fish-liver oils presents special difficulties on account of the decomposition apt to occur at high temperatures. These difficulties have been overcome and vitamin A esters can be prepared in concentrated form on a commercial scale. By molecular distillation of natural oils containing vitamins D and E, these substances also may be concentrated. The application of the process to vitamins D and E is still in the experimental stage.

140. Klose, A. A., and Almquist, H. J.
J. Am. Chem. Soc. 61, 532 (1939)

Received for publication December 19, 1938; issue of February 1939

THE USE OF PHOSPHOTUNGSTIC ACID IN THE PRELIMINARY REFINING OF EXTRACTS CONTAINING VITAMIN K

Vitamin K concentrates are purified by molecular distillation as previously described (Abstract 113).

141. Morton, Avery A.
New York: McGraw-Hill Book Co. (1938) (pp. 118-122)

LABORATORY TECHNIQUE IN ORGANIC CHEMISTRY

The theory and applications of molecular distillation are discussed, and several types of pot stills are described and illustrated.

142. Lovern, J. A., Mead, T. H., and Morton, R. A.
Biochem. J. 33, 338 (1939)

Received for publication January 27, 1939

HALIBUT INTESTINAL OIL

A 0.5-g. sample of oil from the ileum of a relatively fresh halibut was subjected to molecular distillation in a column still, after dilution with 75 ml. constant-yield oil and 75 ml. of residue oil from a previous distillation. Hickman's elimination curve technique was followed, distillate fractions being collected for 10° temperature increments. Spectrophotometric assay showed that about 4 percent of the total vitamin A occurred in the fractions collected over the range 90-140° and that 96

percent was volatile at higher temperatures. The elimination curve over the range 150-240° was tall and narrow with a maximum near 210°. The results indicated that approximately 95 percent of the vitamin occurred as esters and that the acids which were combined in the greater part of these did not differ much in molecular weight.

Distillation of undiluted intestinal oil which had undergone considerable autolysis showed that about 20-30 percent of the vitamin existed in the free state and the free acids accompanied the vitamin in the distillates. The high acid content facilitated cyclization and made it difficult to collect the distillates without overheating the condenser. Another sample from which free acids had been removed was shown to contain 26 percent of the vitamin as free alcohol.

- 143a. Smith, W. Harold, and Wing, Henry J.
J. Res. Nat. Bur. Standards 22, 529 (1939)
Dated January 30, 1939; issue of May 1939

BEHAVIOR OF RUBBER HYDROCARBON IN A MOLECULAR STILL

To obtain information on the molecular weight of rubber it was distilled at 160° in a pot-type molecular still of the Washburn type having an evaporating surface of 60 cm.² and a path of 0.7 mm. During a 100-hour run with a liquid-air-cooled condenser a small deposit was formed which was feebly extensible and did not recover completely when deformed; heating produced a characteristic burned-rubber odor. In further experiments (250 hours, dry-ice condenser, and 140 days, tap-water condenser) the distillates obtained were hard, transparent, and insoluble in ordinary rubber solvents. It was difficult to remove oxygen from the specimens of rubber used, and oxidation or cyclization may have taken place.

- 143b. Smith, W. Harold, and Wing, Henry J.
Rubber Chem. Tech. 12, 789 (1939)

BEHAVIOR OF RUBBER HYDROCARBON IN A MOLECULAR STILL

See preceding abstract.

144. Mead, Thomas H.
Biochem. J. 33, 589 (1939)
Received for publication February 3, 1939

CRYSTALLINE ESTERS OF VITAMIN A. I. PREPARATION AND PROPERTIES

Sterol-free vitamin concentrates from fish-liver oils were purified by repeated fractional molecular distillation in a cyclic still of the Hickman type. The concentrates were diluted with a "residue" oil prepared by removing from cod-liver oil materials molecularly distillable at 250° or less. The distilland was circulated at 6 ml. per minute at temperatures between

85° and 130°. Pressures of 0.001-0.003 mm. were maintained. In an example, a distillate at 95° had a Carr-Price value of 80,000 and $E_{1\%}^{1\text{cm}}$ (328 m μ .) = 1690. In another run a fraction was obtained having $E_{1\%}^{1\text{cm}}$ (328 m μ .) = 1950.

145. Almquist, H. J., and Klose, A. A.
J. Am. Chem. Soc. 61, 745 (1939)

Received for publication February 23, 1939; issue of March 1939

THE ISOLATION OF VITAMIN K AS A CHOLEIC ACID

Molecular distillation was used in preparing some of the vitamin concentrates.

146. Emerson, Oliver H., Emerson, Gladys A., and Evans, Herbert M.
Science 89, 183 (1939)

Issue of February 24, 1939

OCCURRENCE OF GAMMA TOCOPHEROL IN CORN EMBRYO OIL

An oily residue obtained from the sterol-free unsaponifiable of corn oil was molecularly distilled as previously described for palm oil (Abstract 118). The fraction distilling between 120-140° contained the bulk of the tocopherol.

147. Fiaccadori, Alceo
Chimica e industria (Italy) 21, 199 (1939)

Dated February 1939; issue of April 1939

LA DISTILLAZIONE MOLECOLARE

A review of the theory and applications of molecular distillation. Laboratory and industrial-scale apparatus is described and illustrated.

148. Almquist, H. J., and Klose, A. A.
J. Am. Chem. Soc. 61, 1610 (1939)

Received for publication May 19, 1939; issue of June 1939

COLOR REACTIONS IN VITAMIN K CONCENTRATES

Molecular distillation was used for the purification of some of the concentrates.

149. Gray, E. LeB.
J. Biol. Chem. 131, 317 (1939)

Received for publication July 10, 1939; issue of November 1939

Presented before Am. Chem. Soc., April 4, 1939

COMPARISON OF VITAMINS A₁ AND A₂ BY DISTILLATION

Unsaponifiables from Atlantic salmon liver oil were diluted with constant-yield oil and distilled in a cyclic molecular still at temperatures between 100 and 140°. By application of the elimination-curve technique it is shown that the temperature of the vitamin A₂ elimination maximum is only 3° above that of vitamin A₁. This indicates that the molecules of the two vitamins contain the same number of carbon atoms.

150. Almqvist, H. J., and Klose, K. A.
J. Am. Chem. Soc. 61, 2557 (1939)
Received for publication July 21, 1939

SYNTHETIC AND NATURAL ANTIHEMORRHAGIC COMPOUNDS

Solutions of vitamin K, the purified pigment derived from the vitamin by alkaline hydrolysis, the low-temperature distillate from the molecular still (contains no vitamin K), and pure phytol all exhibit a characteristic white fluorescence when exposed to the light from an argon lamp. The active nucleus, 2-methyl-1, 4-naphthoquinone, does not show this fluorescence.

2-Methyl-3(?) -phytyl-1, 4-naphthoquinone was prepared and purified by repeated molecular distillation. The product has the color, oily form and solubilities similar to those of vitamin K from alfalfa and sublimes in the molecular still under the same temperature and pressure. It shows the white fluorescence mentioned above.

151. Morton, Avery A., Mahoney, John F., and Richardson, Graham
Ind. Eng. Chem., Anal. Ed. 11, 460 (1939)
Issue of August 15, 1939

VACUUM SUBLIMATION AND MOLECULAR DISTILLATION APPARATUS

A vertical glass pot still is used for quantities up to 25 g. It consists of an outerjacket 30 cm. long and 6.5 cm. in diameter, having a flange at the top. A bulbous condenser is inserted in a rubber stopper, which is supported by the flange. Contamination of distillates is prevented by use of a glass cloth which is supported just above the distilland. Pressures less than 2×10^{-4} can be maintained.

For smaller quantities of material a sublimation apparatus resembling that of Heilbron et al (Abstract 32) is used. A boat containing the distilland is placed at the closed end of a horizontal tube 75 cm. long and 1.4 cm. in diameter. The open end of the tube is connected by means of a ground joint to the high vacuum system. For most of its length the tube is surrounded by an electric furnace. Just outside the furnace the tube is wrapped with a narrow strip of cloth kept moist and cool; this serves as a condenser. When a fraction is collected at one temperature the electric furnace is moved back about 6 cm., the condenser moved onto the vacant position, the temperature raised a little, and a new fraction collected. The process is repeated until the desired number of fractions has been obtained. Among its uses the apparatus is excellent for testing the purity of a compound, since the first and last fractions should have identical melting points.

152. Gray, E. LeB., Hickman, K. C. D., and Brown, Elizabeth F.
J. Nutrition 19, 39 (1940)

Received for publication August 23, 1939

THE STATE OF VITAMIN A IN THE LIVER OF THE RAT AFTER FEEDING VARIOUS FORMS OF THE VITAMIN

Vitamin A was fed to rats in the form of U.S.P. reference oil, vitamin A caproate, molecularly-distilled ester concentrate, vitamin A stearate, vitamin A alcohol, and β -carotene; 20,000 units were administered over a 48-hour period. The vitamin was recovered in the livers as the esters, using the elimination-curve technique with constant-yield oil, and spectrophotometric assay. Percentage recovery was in the order listed and ranged from 55.6 percent of the vitamin fed as U.S.P. reference oil and 39.3 percent for the free-alcohol form to 9.7 percent from β -carotene. A small amount of the vitamin alcohol was always present, the significance of which is at present unknown. The type of ester in each case was similar, which suggests a selective utilization of fatty acids by the rat for the purpose of esterifying the vitamin.

153. Ahnquist, H. J., and Klose, A. A.
J. Biol. Chem. 130, 791 (1939)

Received for publication September 25, 1939; issue of October 1939

A DERIVATIVE OF VITAMIN K₁

Molecular distillation was used to purify an unknown substance obtained during the alkaline hydrolysis of vitamin K₁.

154. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,234,166

Application November 3, 1939

Patented March 11, 1941

VACUUM DISTILLATION

A new type of centrifugal still comprises an evacuated chamber in which the inner surface of a cone, rotatable on a vertical axis, serves as the evaporator. Within the cone are a series of superimposed condensers. Distillate drains to a receiver below the lowest condenser, whence it is withdrawn to the outside of the chamber. One or several units may be housed in a single evacuated casing. Six claims.

155. Klose, A. A., and Almquist, H. J.
J. Biol. Chem. 132, 469 (1940)
Received for publication December 22, 1939

SYNTHESIS OF VITAMIN K₁

2-Methyl-1,4-naphthoquinone was condensed with phytyl bromide to form vitamin K₁, 2-methyl-3-phytyl-1,4-naphthoquinone. The crude product was fractionated in a molecular still.

156. Fawlings, Herbert W.
Oil and Soap 16, 231 (1939)
Issue of December 1939

MOLECULAR DISTILLATION OF SOYBEAN AND CORN OILS

Alkali-refined soybean oil (1000 gal.) and corn oil (700 gal.) were distilled in a multiple-unit pilot-plant molecular still at a free air pressure of 2×10^{-6} mm. and a rate of 7 to 8 gal. per hour. In the case of soybean oil, 12 percent of distillate was collected in four fractions at temperatures between 170 and 275°C.; the residue was redistilled into three fractions between 280 and 295°, giving an additional 72 percent of distillate. The corn oil was distilled into four fractions (10 percent yield) at temperatures between 180 and 280°C. Analytical data are presented for the distillate fractions and residues.

Successive fractions were increasingly bland, the last being nearly as tasteless as if steam deodorized. Little fractionation of the glyceride constituents occurred, but unsaponifiables were almost completely concentrated in the first two fractions. Pigments and odorous constituents volatilize readily.

157. Furter, M.
Mitt. Lebensm. Hyg. 30, 200 (1939)

NEUE PROBLEME DER DESTILLATION: MOLEKULARDESTILLATION

A lecture reviewing the theory and applications of molecular distillation, with descriptions of apparatus.

158. Anonymous
Osaka, Japan: Boshoku Zasshissha (1939)

NYLON (In Japanese)

A review of Japanese and foreign work on synthetic fibers, including that of Carothers. The Carothers-Hill pot-type molecular still is described and illustrated.

159. Waterman, H. I., and van Vlodrop, C.
Rev. Chim. ind. (Paris) 48, 314 (1939)

LA DISTILLATION MOLECULAIRE OU DISTILLATION A DISTANCE COURTE

A lecture showing the advantages of molecular distillation, especially in the fields of vitamins and hormones, oils and fats, perfumes, petroleum, and light metals. The theory of distillation is outlined. Waterman's work is historically reviewed, and claims to priority in the design and application of various types of stills are presented.

160. Gray, E. LeP., and Cawley, John D.
J. Biol. Chem., 134, 397 (1940)
Received for publication March 11, 1940

THE INFLUENCE OF STRUCTURE ON THE ELIMINATION MAXIMUM. I. THE STRUCTURE OF VITAMIN A₂

By means of the elimination curve technique, the effect of constitution upon the distillation behavior of a number of fatty acids has been determined. A 3-g. sample of a given acid was mixed with 50 ml. of constant-yield oil and 150 ml. of corn oil residue and distilled in a 500-ml. cyclic molecular still, with a 10-min. cycle and 10° temperature increments. For analysis each fraction, in ethanol solution, was titrated against phenolphthalein with 0.1 N aqueous sodium hydroxide.

A comparison of the elimination curves of lauric, myristic, palmitic, and stearic acids shows that one -CH₂- group raises the elimination maximum 5°. Similar comparisons with unsaturated acids show that each unconjugated double bond lowers the maximum 2°; when the double bonds are conjugated, whether in open chains or rings, each additional double bond raises the maximum 3°. As vitamin A₂ has one more conjugated double bond than vitamin A, and its maximum is 3° higher, it probably has the same number of carbon atoms as vitamin A.

161. Gray, E. LeP., Morgareidge, F., and Cawley, J. D.
J. Nutrition 20, 67 (1940)
Received for publication March 12, 1940; issue of July 1940

INTESTINAL ABSORPTION OF VITAMIN A IN THE NORMAL RAT

Vitamin A was fed to rats in the form of its naturally-occurring esters and the percent of free alcohol in the lumen and gut wall determined at various time intervals, using the technique of elimination curves. The data indicate that vitamin A esters behave as do others of the fatty acids in the intestinal tract, in that they are hydrolyzed by the enzymes present there, and further, that during the height of the absorption, the vitamin exists in the gut wall chiefly as the alcohol.

162. Morse, R. S.
Ind. Eng. Chem. 33, 1039 (1941)
Presented before Am. Chem. Soc. April 10, 1940; issue of August 1941

MOLECULAR DISTILLATION OF POLYMERIZED DRYING OILS

The possible application of molecular distillation to polymerized oils such as dehydrated castor, oiticica, walnut, menhaden, and sardine is described. By such a process considerable improvement in film-forming properties is achieved, the drying times, for example, being reduced in some cases by a factor of more than five. A commercial bodied fish oil has been subjected to molecular distillation and chemical and physical analyses made of both the distillates and residues for various percentage distillates.

163. Hickman, Kenneth C. D.
Ind. Eng. Chem. 32, 1451 (1940)
Presented before Am. Chem. Soc., April 11, 1940; issue of November 1940

HIGH-VACUUM DISTILLATION OF THE STEROIDS

Sterols can be separated from the natural oils in which they occur by distillation in the molecular still at 100-220°. The steroids which are not oil soluble are preferably separated by crystallization. If it is desired to distill them, they are best handled as solids in the molecular pot still or in stills of the diffusion type.

Even the sterols which occur naturally in oil are only partially oil soluble. They separate as crystals from the enriched distillates, and after separation of the crystals these distillates can be returned to the molecular still to give new distillates, from which a further crop of crystals can be extracted.

The antirachitic materials formed by the irradiation of sterols are more soluble in oil. They can be separated from the parent sterol by a combination of distillation and crystallization, the antirachitic material remaining in the soluble portion of the distillate.

The molecular still is useful for purifying sterols and waxes isolated in biological research. Small quantities are generally all that are available, and these are handled in the pot still with a detachable head. Although distillation effects concentration of the sterols, it is seldom able to separate them in absolute purity, and must be assisted by saponification and crystallization.

164. Mark, H., and Whitby, G. S.
New York: Interscience Publishers, Inc. (1940)
Dated April 1940

HIGH POLYMERS. VOL. I. COLLECTED PAPERS OF WALLACE H. CAROTHERS

Included is the work of Carothers and associates dealing with the application of molecular distillation in polymer formation. (See Abstracts 19, 25, 26, 27, 28, 29, 41, 42, 43, 44, 45).

165. Riemenschneider, R. W., Swift, C. E., and Sando, Charles E.
Oil and Soap 17, 145 (1940)
Presented before Am. Oil Chem. Soc., May 9-11, 1940; issue of July 1940

MOLECULAR DISTILLATION AND LOW TEMPERATURE CRYSTALLIZATION OF COTTONSEED OIL AND THE STABILITY OF THE MOLECULARLY DISTILLED FRACTIONS

Refined cottonseed oil (1400 g.) was distilled in a Hickman type cyclic molecular still at temperatures between 150 and 250° under an average pressure of .002 mm. Fifteen fractions were collected, having an iodine value spread of 100 to 121. The bulk of the unsaponifiable was concentrated in the first fraction.

Peroxide curves on the distillates showed uniformly decreasing induction periods from fraction 2 to fraction 15. In fraction 1 peroxides were formed at a constant rate which was greater in the early stages (but not in the later stages) than peroxide formation in the other samples. A small amount of sample 1 added to the later fractions decreased their susceptibility to peroxide formation. A composite of all the fractions showed the same characteristics as the original oil, indicating that distillation had not affected the antioxidants or glycerides. Apparently fraction 1 contained the bulk of the antioxidant, but its activity may have been partially masked by the presence of carotene or other easily oxidized substances.

166. Detwiler, Jr., S. B., and Barkley, K. S.
Ind. Eng. Chem., Anal. Ed. 12, 348 (1940)
Issue of June 15, 1940

LABORATORY-TYPE MOLECULAR OR SHORT-PATH STILL FOR VEGETABLE AND ANIMAL FATS AND OILS

An improved column still of the Mair-Schicktz type (Abstr. 71) is described and illustrated. Modifications have been introduced by reducing the number of annuli and receivers, increasing the distribution of distilland over the distilling surfaces, eliminating splashing at the point of ingress of the oil to the column proper, increasing the capacity by enlarging the size of the column, and designing the receiver units to allow for intermittent withdrawal of fractions without interrupting the distillation.

167. Kass, J. P., Loeb, H. G., Norris, F. A., and Burr, G. C.
Oil and Soap 17, 118 (1940)
Issue of June 1940

THE THIOCYANOGEN VALUE OF LINOLENIC ACID

Linolenic acid prepared from hexabromostearic acid was distilled in a molecular still at 10^{-5} mm. pressure.

168. Kaufmann, H. P., and Wolf, W.
Fette u. Seifen 47, 252 (1940)
Issue of June 1940

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UBER DIE ANWENDUNG DER MOLEKULAR-DESTILLATION AUF DEN FETIGEFIEHT. I. DIE
DESTILLATION VON FETTSAUREN UND DIE ENTSAURUNG DER FETTE

A review of the historical and theoretical aspects of molecular distillation. Eighty patents are abstracted. Several molecular stills are illustrated, and results of distillations of various oils are reported. A previous article on the subject is referred to (Kaufmann; Fette u. Seifen 45, 564 (1938)).

169. Baxter, J. G., and Robeson, C. D.
Science 92, 203 (1940)
Issue of August 30, 1940

CRYSTALLINE VITAMIN A PALMITATE AND VITAMIN A ALCOHOL

Vitamin A esters were obtained by distillation of fish liver oils in a cyclic molecular still. After saponification of the concentrates and crystallization of the vitamin alcohol, the latter was esterified with palmityl chloride. After recrystallization of the ester (m. 26-28°)
 $n_{D}^{20} = 1.468$ (328 mm.) = 940.

170. Johnston, W. F., and Bradley, T. F.
Ind. Eng. Chem. 33, 86 (1941)
Presented before Am. Chem. Soc., September 10, 1940; issue of January 1941.

DRYING OILS AND RESINS. PURIFICATION OF POLYMERIZED METHYL LINOLEATE BY MOLECULAR DISTILLATION

The crude dimer of the methyl esters of dehydrated castor oil fatty acids was fractionated in a cyclic molecular still of the Hickman type. A series of fractions was obtained between 180° and 290° at 2×10^{-3} mm. The bulk of the distillate comprised one or more dimers of methyl linoleate which were redistilled at 190-200°. The polymerization of methyl linoleate appears to be analogous to the dimerization and trimerization of butadiene.

171. Kaufmann, H. P., and Wolf, W.
Fette u. Seifen 48, 51 (1941)
Issue of February 1941

ÜBER DIE ANWENDUNG DER MOLEKULAR-DESTILLATION AUF DEM FETTGEBIET. II. DIE
DESTILLATION VON GLYCERIDEN

Detailed results of the molecular distillation of a number of fats are described. Included are triolein, trimyristin, coconut fat, palm kernel fat, butterfat, linseed oil, and soybean oil. As a typical example, crude soybean oil (IV 124.7) was separated into four fractions at temperatures up to 255°, 261°, 264°, and 267°, having iodine values of 116.9, 121.4, 124.1, and 128.0, respectively. The residue (15 percent) had an IV of 118.5.

172. Hickman, Kenneth, and Nees, Graham C.
Abstracts of Papers, 101st Mtg. Am. Chem. Soc. B-7 (1941)
Presented before Am. Chem. Soc., April 7, 1941

VITAMIN A SUPPLIES DURING A NATIONAL EMERGENCY

Expansion now under way in machinery for the concentration of vitamin A by molecular distillation, should prevent a shortage of the vitamin during the current emergency.

173. Embree, Norris
Abstracts of Papers, 101st Mtg. Am. Chem. Soc. B-26 (1941)
Presented before Am. Chem. Soc., April 9, 1941

THE SEPARATION OF NATURAL COMPONENTS BY MOLECULAR DISTILLATION

Molecular distillation permits successful concentration of vitamin K, the natural fatty acid esters of vitamin A, vitamin D, the sterols, and other alkali-sensitive unsaponifiable material. In the distillation of animal or vegetable oils, odoriferous materials, free fatty acids, and unsaponifiables are usually concentrated in that order in the early fractions. The later fractions usually consist of pure triglycerides.

The triglyceride composition is substantially the same in each fraction from the distillation of soybean oil. No better separation is made with cottonseed oil, castor oil, or corn oil. Slightly better separation is made with linseed oil, and a marked separation is made with the glycerides of coconut and menhaden oil.

174. Quackenbush, F. W., Gottlieb, H. L., and Steenbock, Harry
Abstracts of Papers, 101st Mtg. Am. Chem. Soc. A-11 (1941)
Presented before Am. Chem. Soc., April 8, 1941

DISTILLATION OF TOCOPHEROLS FROM SOYBEAN OIL

An all-glass cyclic molecular still was designed for the separation and concentration of small amounts of material. Under the conditions employed, the distillation maximum of pure α -tocopherol was found to be 140° ; α -tocopherol was recoverable without loss in the distillate.

An attempted distillation of vitamin E from crude soybean oil showed a distillation maximum slightly lower than 140° , suggesting the presence of a mixture of tocopherols. Of the total tocopherol present as determined photometrically, less than half distilled below 220° . The remainder of the chromogenic substances was shown to remain quantitatively in the undistilled residue.

175. Gray, E. Leb., and Cawley, John D.
Abstracts of Papers, 101st Mtg. Am. Chem. Soc. A-10 (1941)
Presented before Am. Chem. Soc., April 8, 1941

THE STATE OF VITAMIN A IN THE LIVER OF THE RAT. II. THE EFFECT OF FEEDING THE VITAMIN OVER EXTENDED PERIODS

Previous work (Abstr. 152) showed that vitamin A fed to rats over a short period of time was recovered in the livers as a complex mixture of esters. It has now been found that when the same amount of vitamin is fed over an extended period of time, the complexity of the ester mixture, as judged by the elimination-curve technique, is diminished. If the time period is sufficiently long, a point is finally reached where but a single ester is present in substantial amounts. This ester is apparently characteristic of the animal rather than the material fed.

176. Earle, F. R., and Detwiler, Samuel B., Jr.
Oil and Soap 18, 117 (1941)
Issue of June 1941

WAX CONSTITUENTS OF THE WINTERIZER PRESS CAKE OF SOYBEAN OIL

An improved pot-type molecular still was used to separate free alcohols from waxes found in the winterizer press cake of soybean oil. An attempt was also made to fractionate the waxes. The apparatus is described and illustrated.

SUPPLEMENT NO. 1 TO ABSTRACTS OF PATENTS AND JOURNAL
ARTICLES RELATING TO MOLECULAR DISTILLATION

177. Cloetta, M.
Arch. exptl. Path. Pharmacol. 88, 113 (1920)
Issue of November 5, 1920

ZUR KENNNTNIS DER CHEMIE UND PHARMAKOLOGIE DES DIGITOXINS UND SEINER
SPALTUNGSPRODUKTE

Small quantities of digitoxin were purified by sublimation in a glass vessel connected through a ground joint to a mercury vapor pump. Pressures were estimated by means of a spark discharge. On heating, the distilland in a metal bath at 270° a white, crystalline distillate was formed in the upper part of the vessel.

178. Hickman, Kenneth C. D., and Hecker, John C. (to Distillation Products, Inc.)
U. S. patent 2,249,524
Application January 27, 1939
Patented July 15, 1941

PROCESS FOR IMPROVING OILS

Substances of undesirable odor and taste are removed from vitamin-containing oils by subjecting such oils to short-path distillation to remove a fraction containing between 0.5 and 2 percent of the vitamin content. The purified oil is then withdrawn from the still as undistilled residue. Two claims.

179. Hickman, Kenneth C. D. (to Distillation Products, Inc.)
U. S. patent 2,249,526
Application June 9, 1939
Patented July 15, 1941

VACUUM DISTILLATION

Molecular distillation residues are treated to mechanically separate solids contained therein and formed by the distillation. The liquid so treated is then re-subjected to distillation. Six claims.

180. Distillation Products, Inc.
British patent 526,389
Accepted September 17, 1940

VITAMIN COMPOSITIONS

The oil is submitted to a preliminary saponification by use of an amount of saponifying agent in excess of that required to saponify the free fatty acid content of the oil but not exceeding 20 percent excess. The oil is siphoned off from the settled mixture and filtered through a siliceous filter bed. After degassing, the oil is subjected to distillation in a small high-vacuum still having vaporizing and condensing surfaces separated by about one inch. (From Chemical Abstracts 35:7123; patent not at hand.)

181. Distillation Products, Inc.
British patent 527,381
Accepted October 8, 1940

TREATING ANIMAL AND VEGETABLE OILS FOR RETARDING OXIDATION

The oils are subjected to high-vacuum unobstructed-path distillation. A distillate fraction is collected in a known manner possessing antioxidant properties and the first one to two percent of distillate is separated therefrom as a separate fraction possessing pro-oxidant properties. (From Chemical Abstracts 35:7224; patent not at hand.)

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- Chaudron, G., and Garvin, M. *Chimie et industrie* Special No. 218, 430 (Sept. 1926). (CA 21:514)
- Chaudron, G., and Garvin, G. *Chimie et industrie* Special No., 386 (April 1928). (CA 22:4384)
- Hérenghuel, J., and Chaudron, G. *Compt. rend.* 193, 771 (1931). (CA 26:663)
- Hérenghuel, J., and Chaudron, G. *Compt. rend.* 195, 1272 (1932). (CA 27:1301)
- Chaudron, G., and Hérenghuel, J. French patent 751,085, August 26, 1933. (CA 28:1009)
- Hérenghuel, J. *Chimie et industrie* Special No., 701 (April 1934). (CA 28:5379)
- Hérenghuel, J., and Chaudron, G. 14th Congr. chim. ind., Paris, Oct. 1934, 5 pp. (CA 29:6188)
- Hérenghuel, J., and Chaudron, G. *Métaux* 9, 415 (1934). (CA 29:7892)

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406,148 Imperial Chemical Industries 47e

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| 477,955 | Kodak, Ltd. | Abstract | 90a |
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| 480,265 | Fawcett, Burrows, Imperial Chemical Industries | | 96a |
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| 481,189 | Kodak, Ltd. | | 77d |
| 482,380 | Kodak, Ltd. | | 91a |
| 482,881 | Kodak, Ltd. | | 92a |
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| 485,549 | Eastman Kodak Co. | | 66b |
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| 493,948 | Kodak, Ltd. | | 105 |
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| 501,841 | Eastman Kodak Co. | | 88b |
| 507,471 | Kodak, Ltd. | | 117 |
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| 709,974 | N. V. de Betaafsche | | 17d |
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| 817,036 | Eastman Kodak Co. | | 79c |
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German

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