MOLECULAR DISTILLATION CHARACTERISTICS OF SEVERAL ANTHRAQUINONE DYES

by

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I. INTRODUCTION

The distillation of substances of higher molecular weights such as organic oils, dyes, and drugs requires special equipment from that available for ordinary distillation. Study in the resulting field, high-Vacuum distillation, has subsequently led to the development of such equipment. Three types of high-vacuum distillation are recognized: conventional distillation, unobstructed-path distillation, and molecular distillation.

Molecular or short-path distillation occurs when the vapor path is unobstructed and the condenser is separated from the evaporator by a distance less than the mean free path of the evaporating molecules. Molecular distillation is the limiting type of high vacuum distillation with the absolute pressure range approximately 1 to 7 microns of mercury. The use of the centrifugal molecular still permits the distillation of organic substances which might suffer thermal decomposition even under the conditions of the conventional high vacuum still. Problems of molecular distillation include reducing heat requirements and the complex vacuum equipment which must be used to obtain the required vacuum.

Against the advantages of prevention of thermal decomposition and shorter time requirements must be placed the poor separatory power of distillation in the molecular still. In order to obtain relatively pure substances from a mixture of two or more organic compounds, a series of redistillations must be performed in the same or in a group of separate stills. A study of the elimination curves is necessary to determine the best methods of operating molecular stills for the production of purer substances. These curves plot the yield of a component during distillation against the temperature of distillation during which this yield is occurring.

The purpose of this investigation was the determination of the elimination curves of single anthraquinone dyes and binary and tertiary mixtures of these dyes and the separation of binary mixtures of dyes by redistillative methods.

II. LITERATURE REVIEW

A review of the available literature was made to obtain an understanding of the development and operation of molecular distillation. The terminology, development, theory, performance, and evaluation of still performance of molecular distillation will be considered.

Terminology of Molecular Distillation

The terminology of molecular distillation and differences between ordinary distillation, normal high-vacuum distillation, and molecular distillation are considered primarily through definition and explanation of the special nomenclature of the field.

Distillation. Carey(14) defines distillation as "the separation of the constituents of a liquid mixture by partial vaporization of the mixture and separate recovery of vapor and residue. The more volatile constituents of the original mixture are obtained in increased concentration in the vapor; the less volatile in greater concentration in the liquid residue." In general, the term, distillation, is applied to any vaporization processes in which the vapor evolved is recovered, usually by condensation.

High-Vacuum Distillation. Hickman(38) defines three broad classes of high-vacuum distillation according to the method and equipment employed: (1) conventional or nearly conventional apparatus, generally consisting of a boiler, fractionating column, and condenser, operated under high vacuum; (2) unobstructed-path distillation operated under high or nearly high vacuum; and (3) molecular distillation or "projective distillation" where the vapor path is unobstructed and the condenser is separated from the evaporator by a distance less than the mean free path of the evaporating molecules. Thus, only one class of high-vacuum distillation can actually be considered as true molecular distillation while the others are merely approaches to molecular distillation.

Molecular Distillation. Molecular distillation received its name from the fact that vaporization is carried out in such a vacuum that almost every molecule travels toward the condensing surface unhindered by the presence of other molecules. There is a minimum return of once vaporized molecules to the main body of the liquid. As in other high-vacuum distillation, only the molecules at the evaporating surface enter into the process, and, at any given instant, all other molecules in the bulk of the distilland need not be considered as part of the distilling process except as they replace the evaporating molecules(9). Trouble arises with the "spontaneous refusal of liquids to evaporate at rates and temperatures appropriate to them" due to the repressive "skin" layer of surface molecules. This has resulted in the development of falling-film and centrifugal molecular stills to prevent the sudden explosion of the repressive skin in the vacuum pot still.

Basic Differences in Distillation Processes. In conventional distillation processes(14), distillation begins at a well defined temperature, the material being distilled has a definite boiling point, and the distillation process is accomplished by ebullition or boiling of the distilland. A dynamic equilibrium exists between the liquid and vapor phases causing a large proportion of the molecules evaporating from the liquid surface to return to the same liquid surface.

On the other hand, in high-vacuum distillation processes, there is no well defined temperature at which distillation begins. Some distillation occurs at any temperature as long as a thermal gradient exists between the condenser and the evaporator. Due to the high vacuum maintained during the process, there is effectively no superincumbent air pressure on the material being distilled and, consequently, there is no well defined boiling point or attending ebullition of the distilland. The distilling vapor molecules pass directly from the vaporizing surface to the condensing surface without having to pass through a barrier of gas molecules. The number of distilling molecules returning to the liquid phase can be considered insignificant in comparison to conventional distillation.

As a consequence, dynamic equilibrium between vapor and liquid cannot exist during high-vacuum distillation. Molecular distillation has thereby become known also as "nonequilibrant" distillation.

High Vacuum. Hickman(38) considered "high vacuum" as the existence of a pressure of residual gas so low that further reduction does not change the performance of the apparatus. Andersen(1) has also suggested a more restrictive meaning for high vacuum than it has in ordinary usage in that "high vacuum" should be considered to exist only when the pressure is sufficiently low that the mean free path of the vapor molecules in the residual gas is of the same magnitude as the size of the container. It is apparent that what might constitute high vacuum in one piece of equipment does not necessarily constitute high vacuum in another. For example, in a vessel one foot in diameter, the absolute pressure may be at least 0.2 micron while for a vessel ten feet in diameter, the pressure must be less than 0.02 micron. Such a definition of high vacuum would limit it to molecular distillation as vessels used in this field are generally of the magnitude of the mean free path of the distilling molecules.

The units of pressure adopted for high-vacuum work are millimeters of mercury and microns of mercury, one millimeter equal to 1000 microns. Molecular distillation is generally conducted at pressures of 1 to 7 microns of mercury with industrial molecular distillation employing an absolute pressure of about 3 microns as the economical level below which the added cost of vacuum equipment and operation is not warranted by the benefits that result.

Distillability. The rate of distillation of a substance is roughly proportional to its concentration and its vapor pressure for conventional distillation. For molecular distillation, the rate of distillation is proportional to the product of the number of molecules and the probability that any molecule will distill(32). This probability or tendency to distill is called the "distillability". The "distillability" has also been defined "as the ratio of the number of molecules of a given species leaving the distilling surface in any small interval compared with the number of similar molecules remaining undistilled in the surface layer during the same interval"(41).

Mean Free Path. Glasstone(37) defines the mean free path of a molecule as the average distance a molecule moves between two successive paths or successive collisions. Since molecular distillation tends to reduce collisions between molecules (increase the mean free path) by use of high vacuum, the theory of the mean free path is most important in this field.

Maxwell's expression(37) for the calculation of the mean free path is:

$$l = V/\pi\sqrt{2}\,N\sigma^2$$

where:

l = mean free path, centimeters

N = Avagadro's number, 6.06×10^{23}

V = volume of one gram mole of the gas at the existing pressure, cubic centimeters

σ = average diameter of a gas molecule, 2×10^{-8} centimeters

π = a constant

This expression takes into account the relationship between relative velocity and actual velocity when a number of molecules all in motion are present, but is limited by the assumption of an average diameter for all the gas molecules.

Distilland, Distillate, and Residue. In molecular distillation, the feed mixture to be distilled is referred to as the "distilland". The "distillate" is that portion of the "distilland" removed as vapor and condensed, and the "residue" is the undistilled portion of the "distilland".

Development of Molecular Distillation

Although molecular distillation had been until the past two decades a laboratory technique used exclusively for research, it has since been extended to the processing of industrial chemicals at rates approximating a million gallons annually(49). Numerous bibliographical references(29, 30, 46, 58) to the development of molecular distillation are available.

Historical. The need for a better type of still for organic chemicals became evident to chemists in the period from 1910 to 1925, when substances of ever-increasing molecular weight and boiling point were coming under study(39). Bronsted and von Hevesy(4) appear to have designed the first molecular still to separate the isotopes of mercury in 1922. The first application of molecular distillation to organic chemicals, and the first comprehensive statement of the potentialities of the operation were made by Burch(10, 11) in England. Both Waterman(60), who applied molecular distillation to labile substances in Holland, and Washburn(59), in the United States, were responsible for important early developments in molecular distillation.

Following the pioneer laboratory development of molecular distillation in the early 1920's, the Eastman Kodak Company undertook considerable development work in the 1930's in relation to a high-vacuum process for the drying of photographic film. This work led to the development of high-vacuum condensation and fractionating pumps, the lack of which had hindered the progress of molecular distillation. In 1934, the Eastman Kodak Company joined with General Mills, Incorporated, to organize a joint subsidiary, Distillation Products, Incorporated, for the processing of oil soluble vitamin concentrate by molecular distillation. The first industrial use of molecular distillation was the separation of vitamins A and E from marine and vegetable oils.

Types of Stills and Their Development. As more efficient stills have been developed from the crude pot stills employed by the first experimenters, it became evident that molecular distillation would find valuable applications beyond the relatively narrow confines of the vitamin industry. The development of the molecular still has progressed through three prominent stages(39): (1) the pot still with a "boiling" flask similar to that employed in conventional distillation but operating under high vacuum and with a condenser relatively close to the "boiling flask", (2) the falling-film still where the distilland is metered to the vacuum chamber, degassed, and allowed to pass in a thin film down the walls of the evaporator, and (3) the centrifugal still where the distilland is metered to and passes over a rotor generally housed in a bell jar and supported on a shaft to the motor drive.

Table I, page 26, shows the transition from the earliest pot still to the centrifugal stills giving the approximate dates when each type of still was developed and the film thicknesses and times of exposure encountered in each still.

Distillation Products, Incorporated, has offered for sale large centrifugal molecular stills designed to handle 50 to 250 gallons per hour of oils or heavy chemicals(51). These stills utilize a rotating evaporator five feet in diameter and shaped like a flower pot. Separatory distillation is reputed to be from 2 to 3 times better than that obtainable from a pot-type still.

Applications of Molecular Distillation. Molecular distillation has rendered distillable a whole category of substances, natural and synthetic, which could not be distilled otherwise primarily because of thermal decomposition at the high temperatures required. The range of usefulness of the molecular still is for organic chemicals of molecular weights between 250 and 1200 with a lower range if much oxygen, sulfur, or halogens are present in the molecules(49).

It would be impractical to attempt to give a complete list of all the specific applications of molecular distillation which have been reported. However, a list of materials to which the technique has been applied might be classified under the following headings(30):

TABLE I

Transition from Pot Still to Centrifugal Still

Approximate Date	Type of Still	Approximate Distilland Thickness [a]	Molecular Thickness[b]	Approximate Time of Exposure
1922	Laboratory Pot Still	1-5 cm	5×10^7	1-5 hr
1928	Laboratory Tray Still	0.1-1 cm	5×10^6	5-60 min
1930	Laboratory Falling-Film Still	0.1-0.3 mm	5×10^4	10-50 sec
1935	Industrial Falling-Film Still	1-3 mm	5×10^5	2-10 min
1936	Laboratory Centrifugal Still	0.01-0.02 mm	3×10^3	0.04-0.08 sec
1940	Industrial Centrifugal Still	0.03-0.06 mm	1×10^4	0.1-1 sec
1942	High-Speed Centrifugal Rim Still	0.001-0.005 mm	4×10^2	0.001-0.005 sec

[a] Assuming similar throughput for same unit area of all stills.

[b] Assuming that the molecule of glyceride fat has an effective diameter of 15 Å.

Hickman, K. C. D.: "Science in Progress," p. 217. Yale University Press, New Haven, Conn., 1945. Fourth Series.

Vegetable, animal, and marine oils for edible and drying oil purposes

Solid fats

Petroleum oils and jellies

Long-chain hydrocarbons

Aromatic hydrocarbons and derivatives

Vegetable and fruit waxes

Carbohydrates

Vitamins

Sterols and sterol esters

Hormones

Saponins

Amino acids, polypeptides, and derivatives

Condensation polymers

Phythaloyl esters

Dyes

Drugs

Miscellaneous substances such as digitonin, cholanic acid, querbrachol, fungoid growths, and others.

Further information on the application of molecular distillation can be found in the abstracts of Detwiler and Markley(30, 31) and Todd(57) and the bibliographies of Hickman(46), Blasco(3), Burch(12), Fawcett(35), Burrows(13), and Waterman and van Vlodrop(60).

Theory of Molecular Distillation

In considering the theory of molecular distillation, several factors are of importance; the rate of distillation, the film thickness, the thermal hazard, the limitations encountered, and the mean free path considerations involved.

Rate of Distillation. For conventional distillation, the rate of distillation of any individual substance is roughly proportional to its concentration and to its vapor pressure. In molecular distillation, heat is supplied to the distilland as under equilibrium conditions but the majority of the molecules leaving the evaporator are collected almost immediately on the condenser. Thus, the rate of heat input at a constant temperature and the shape of the still are not significant variables as in the case of conventional distillation. In molecular distillation, the rate of distillation is proportional to the product of the number of molecules and the probability that each molecule will distill. This tendency to distill has been termed the "distillability". Embree(34) gives a more exact but less illuminating definition of the "distillability" of a substance as being "proportional to its rate of distillation divided by its concentration". He states that "the rate of distillation of a substance is proportional to the product of its concentration and its distillability".

Expressed algebraically this becomes,

$$V = kND$$

where:

V = rate of distillation, moles per second

k = proportionality constant

N = concentration, mole fraction

D = distillabiltiy.

If the distilland is considered to be an ideal solution, the partial pressure, p, of the substance considered may be taken as the product of N and P, the concentration and the vapor pressure of the pure substance, respectively. The rate of distillation by Langmuir's equation then becomes,

$$n = NPA \frac{1}{2 \ MRT}$$

where:

n = rate of distillation, moles per second

N = concentration, mole fraction

P = vapor pressure, dynes per square centimeter

A = area of distilling surface, square centimeters

M = molecular weight

R = ideal gas constant

T = temperature, degrees Kelvin.

For any one still this term becomes $n = kNP/T$ when the constant terms are considered. The distillability for this case is then proportional to P/T. As an approximation, the distillability may be considered to vary directly with the vapor pressure of the substance since the changes in $1/T$ are small compared to changes in P.

Bronsted and von Hevesy(4) found that the rate of distillation of the components of a mixture was inversely proportional to the square root of the molecular weights of these components as indicated by the Langmuir equation. Washburn et al(59) observed that the equation was valid for solutions if no recondensation occurred on the evaporating surface. The actual rate of distillation will always be less than the theoretical because of the return of some molecules to the evaporating surface. Langmuir(56) found that under even the worst conditions, reflection, or return of the molecules to the evaporating surface, will not be greater than 90 per cent so that the actual rate can never be less than 10 per cent of the calculated rate. Burch and van Dijck(12) postulated and Fawcett(35) verified the theory that if the residual gas pressure was made sufficiently low that molecular distillation occurred, further reduction of pressure would effect no change in the rate of distillation.

Surface Layer and Film Thickness. A most important factor in molecular distillation is the surface of the distilling liquid(49). It must be remembered that only this surface is involved in the distillation. Momentarily, none of the other molecules in the still need be there. The only reason they are in the still at all is to replenish the surface layer. While only the molecules that are at the surface are needed for distillation, all the molecules waiting their turn in the still are at the same temperature and thus, exposed to thermal decomposition. The reasoning behind a desire for a thin film thickness is evident.

A formula(46) for the relationship between the rotor speed and film thickness for centrifugal stills may be expresses as:

$$\log u = K \frac{1}{\log L}$$

where:

u = velocity, revolutions per minute

K = proportionality constant

L = film thickness, millimeters.

This formula was determined through a study of the spiral streams caused by feeding both colored and colorless oils slightly off rotor center and at the rotor center, respectively. Since the colored oil was applied eccentrically, it formed a small separate stream within the main colorless stream and the composite pattern of alternate colored and colorless spirals proceeded outward from the center of the rotor. The thickness at any position was determined to be directly proportional to the distance between the spirals and inversely proportional to the area of the particular portion of the rotor considered. The persistence of the spiral pattern across the rotor is interpreted as indicating that the distilland is present in such a thin film that the evaporating surface at any moment represents the composition of the film beneath. The diffusion is so rapid that all of the molecules will come to the surface at some time during the travel across the rotor. According to Fawcett(35), a concentration gradient will be set up through the film if the rate of evaporation is greater than the rate of diffusion to the outer layer. A concentration gradient will be of importance in decreasing the efficiency of the process because (1) the gross rate of evaporation will decrease as the more volatile constituents are stripped out and the vapor pressure decreased, and (2) the fractionating power will decrease since excessive quantities of the less volatile will appear in the distillate and the more volatile will appear in the residue.

Thermal Hazard. The greatest advantage of high-vacuum distillation is the ability to distill successfully substances of high molecular weight which are thermally unstable at temperatures which would be required by conventional distillation. The thermal hazards become increasingly more important as the size of the molecule becomes larger. The quantity of distilland being heated and the time of heating contribute to the thermal exposure. Hickman and Embree(53) have developed a "hazard index" concept and have tabulated the thermal exposure of various stills, Table II, page 34. According to the hazard index, the decomposition hazard, D, is the product of the time, t, in seconds of exposure and the pressure, P, in microns of mercury, or:

$$D = t \times p.$$

It will be noted that the thermal hazard encountered with thin-film distilland in the centrifugal molecular still is far less than with any other type of still.

Limitations of Molecular Distillation. In ideal molecular distillation, equilibrium does not exist between the vapor and the liquid with no molecules reentering the distilland after being vaporized. As indicated by the Langmuir equation, the quantity of a given material distilling at a given temperature is proportional to P/M where P is the vapor pressure and M is the molecular weight. The relative quantities of two or more substances distilling from a mixture are,

$$P_1/M_1, P_2/M_2, \ldots\ldots\ldots\ldots\ldots\ldots P_n/M_n.$$

TABLE II

Thermal Exposures of Various Stills

Kind of Still	Pressure mm Hg	Time	Temperature[a] °C	Relative Thermal Coefficient[b]	Relative Decomposition Hazard
Simple Flask	760	1 hr	360	2^{23}	1.5×10^{12}
Claisen Flask	10	1 hr	270	2^{14}	3.0×10^{9}
Wide-Neck Pot Still	1	1 hr	220	2^{9}	9.2×10^{7}
Petroleum Flash Still	1	1 min	220	2^{9}	1.5×10^{6}
Molecular Pot Still	0.001	1 hr	130	1	1.8×10^{5}
Molecular Falling-Film Still	0.001	1 min	130	1	3.0×10^{3}
Molecular Centrifugal Still	0.001	1 sec	130	1	5.0×10^{1}
Molecular Centrifugal Still	0.001	0.02 sec	130	1	1.0

[a] Boiling points of dibenzylphthalate, for example.

[b] Assuming that the hazard doubles with each 10 °C rise.

Hickman, K. C. D. and N. D. Embree: Decomposition Hazard in Vacuum Stills, Ind. and Eng. Chem., <u>40</u>, 135 (1948).

This property of molecular distillation makes it impossible to separate, by a single distillation, two substances having $P_1/M_1 = P_2/M_2$. In many molecular distillation operations, where the vapor pressure and/or the molecular weight of the constituents do not differ radically, distillation simply increases the concentration of one constituent rather than giving a sharp separation. The molecular still is valuable not because it gives good separation but because distillation is accomplished at much lower temperatures from 50 to 250 degrees Centigrade below temperatures encountered in conventional distillation(50).

Azeotropic mixtures which cannot be readily separated in an ordinary still may be separated by molecular distillation if their molecular weights are different. The degree of separation effected is due to the fact that although the constituents are evaporating simultaneously, they are each evaporating at different rates.

<u>Mean Free Path Considerations</u>. Vaporized molecules leaving the evaporating surface will necessarily be delayed in reaching the condensing surface or may even return to the distilland if they suffer collisions with other molecules. Any delay of the emergent molecules in reaching the condenser would result in distillation becoming more equilibrant and one would expect reduced distillation rates. Hickman(39) measured the change in rates of

distillation with changes in the pressure of the residual gas and found that collisions had less effect than might be expected. Table III, page 37, gives the mean free paths and relative rates of distillation for various residual gas pressures. It will be noted that the rate of distillation is reduced by less than 40 per cent for a change from 80 to 0.005 per cent in the number of molecules reaching the condenser without collision.

Various formulas for the mean free path of like molecules and molecules in the presence of unlike molecules have been developed. Maxwell's expression for the calculation of the mean free path has been considered in a previous section on terminology of molecular distillation. The calculation for large nonspherical molecules using this and other formulas gives mean free paths which are likely to be in error. There is some indication that such oil molecules as amyl phthalate and amyl sebacate have "undeflected mean free paths" several times longer than those calculated by classical theory(39).

TABLE III

Comparison of Pressure, Free Path, and Rate Of Distillation in a Molecular Still

Pressure of Residual Air in 2 Cm Gap	Two Cm Gap is Approximate Multiple m of Free Path	Comparative Distillation Rate with Saturation Pressures of		Number of Molecules Reaching Condenser Without Collision
		1 µ	10µ	
µ		%	%	%
0.3	0.2	100	100	80
4.0	3	77	89	--
7.0	5	63	81	0.005
10.0	7	53	72	--
25.0	17	35	42	--
50.0	33	20	27	--

Hickman, K. C. D.: Molecular Distillation, "Chemical Engineers' Handbook" (J. H. Perry, Editor), p. 656. McGraw-Hill Book Co., Inc., New York, N. Y., 1950. 3 ed.

Variables Affecting Molecular Distillation

In molecular distillation, the rate of distillation of any component and the degree of separation of the components of a mixture depend on a number of interdependent variables in the design and operation of the still(36). Meaning can only be given to experimental results from the laboratory distillation of substances when arbitrary distillation conditions are fixed by close control of the variables affecting distillation. These variables include operating pressure, temperature of distilland, film thickness, splashing, rotor speed, angle of inclination of rotor surface, temperature of condensing surface, and distance between evaporator and condenser.

Operating Pressure. In true molecular distillation, the rate of evaporation is independent of pressure. Once the residual gas pressure in the still equals the vapor pressure of the distilland at the temperature of operation, further reduction in pressure effects no further increase in the rate of distillation. If the residual gas pressure within the still is allowed to exceed the vapor pressure of the distilland, a reduction in the rate of distillation will occur. As the pressure in a still rises, operation will approach equilibrant high-vacuum evaporation rather than molecular distillation with the distillation rate becoming a function of the vapor pressure alone.

Temperature of Distilland. The measurement of the temperature of the actively distilling surface of the distilland presents a problem which has not been satisfactorily solved. There exists a temperature gradient of about five degrees through the distilland in a falling-film still(35). The temperature gradient is probably less in the centrifugal molecular still because of the decrease in film thickness. There is also a temperature gradient from the center of the rotor to the outer rim which varies with the feed temperature and heat applied on the rotor. The customary practice has been to control the average temperature of the distilland by use of a source of heat at a constant rotor temperature and a constant temperature difference between the evaporator and the condenser. The average temperature of the distilland of a centrifugal molecular still may be estimated by inserting a thermocouple in the collecting gutter.

Increasing the temperature of distillation increases the vapor pressure of the distilland and hence the rate of distillation. However, it should be recalled that the increase in distilling temperature causes a secondary effect of reducing the mean free path which would ordinarily be expected to reduce distillation. In general, this slight reduction in the rate of distillation will be much more than compensated by the increase resulting from increased vapor pressure. According to Fawcett(35) the highest gross distillation will occur at the highest possible temperature short of decomposition even though the distillation may shift from the molecular to the non-molecular type.

Film Thickness of Distilland. The exact effect of the film thickness on molecular distillation is unknown. Recent still design has attempted to reduce the film thickness in order to insure that diffusion will take place sufficiently rapidly to make the surface or distilling layer representative of the fluid beneath.

The theory of the surface layer and calculations for film thickness have been considered in the section on the theory of molecular distillation.

Splashing. Splashing will affect the degree of separation obtainable in molecular distillation since substances of lower volatility will be carried into the distillate. One of the chief reasons for the use of a thin film is to assist in the prevention of splashing of the distilland. The maintenance of a thin film on the rotor will not by itself insure the absence of splashing, but it does aid greatly in degassing of the distilland. Improper degassing and too rapid evaporation have been mentioned(46) as the major causes of splashing. Too rapid evaporation would likely occur if the heat input to the distilland and the subsequent temperature of distillation were higher than necessary for proper distillation.

Rotor Speed. Hickman(48) found that increasing the rotational speed of the evaporator from 100 to 3000 revolutions per minute quadrupled the amount of distillate collected on the condenser. It was first supposed that friction was the cause or that the metallic rotor was reacting with the electrical heating coil behind. Neither of these was found to be the reason for increased distillation. The real reason proved to be the changing radiative properties of the oil in thin layers. When an oil is spread sufficiently thin on the rotor, the loss of radiant heat is reduced considerably. If the film of distilland is sufficiently thin it will, for all practical purposes, cease to emit radiation. The importance of the rotor speed as well as the feed rate on the film thickness, and therefore, on still performance, is evident.

Angle of Inclination of Rotor Surface. Tests made by Coli(27) using rotors with angles of inclination of rotor surface of 52-1/2, 60, 67-1/2, and 75 degrees indicated no overall effect on the separation. A difference might have been expected with the difference in gradient of the distilland on the rotor but was not evidenced.

Temperature of Condensing Surface. The primary consideration of the condensing surface is that it be at a temperature sufficiently below that of the distilling surface to prevent any revaporization of the distillate on the condenser(37, 59). Any further reduction in the condenser temperature will not improve either the rate of distillation or condensation. Commercial units are generally not provided with any external means of cooling the bell jar condensing surface(47, 54). Often cooling coils or baffles are provided inside the bell jar to assist in condensation or in special fractionation of the distillate by partial condensation.

Distance Between Evaporator and Condenser. The mean free path considerations have been discussed in a previous section. In general, variations of the gap between the evaporator and the condenser do not produce any very noticeable variations in still performance provided that the gap does not become much larger than the mean free path(35). It is also possible that the gap may be reduced to such an extent that the distillation rate will be decreased. Distillation tests made using linseed oil with gaps varying from 1 to 6 centimeters showed no significant change. A gap of 0.5 centimeter resulted in decreased distillation. The closeness of the condenser to the evaporating surface tended to permit the return of some of the vaporized molecules to the distilling surface which would not have returned otherwise.

Evaluation of Still Performance

The fractionating ability of molecular stills is best evaluated in terms of the theoretical molecular plate. The distillation of individual substances is usually illustrated by means of individual and composite elimination curves. The uses of pilot dyes and constant-yield oil in molecular distillation studies are also discussed.

Theoretical Molecular Plate. The unit of separation that a single passage can theoretically achieve is considered to represent one theoretical molecular plate(51). A separation equivalent to one theoretical molecular plate is assumed to occur when the condenser is infinitely close to the evaporator, distillation is sufficiently slow that the composition of the evaporating surface is representative of the main bulk of the distilland, and the vapor molecules emerge sufficiently far apart from one another in time and space that there are no collisions in travel. The maximum difference in composition of distilland and distillate vapor would occur under such conditions. The Langmuir equation could then be used to determine the separation of binary mixtures as proportional to the ratio of the partial pressures and to the square roots of the molecular weights of the constituents.

The concept of the theoretical molecular plate in centrifugal molecular distillation is somewhat analogous to the theoretical plate in equilibrant distillation although the concept becomes complicated by the progressive travel of the film across the rotor. In the well-stirred pot still, it is assumed that every element of evaporating area is of identical composition. In the centrifugal still, however, succeeding areas cannot be identical in composition except at an infinite ratio of evaporation to throughput.

Industrially, centrifugal molecular stills have been reported as giving separations of 0.80 to 0.95 theoretical molecular plate(52). Such separations are 2 to 3 times better than that obtainable from nonfractionating pipe or pot stills. Stills using fractionating barriers, partial condensers, and other devices for giving better separation can be described as having separating ability of multiples of the theoretical molecular plate.

Analytical Distillation. In conventional distillation, the boiling point(42) of a substance is the temperature at which its vapor is equal to a specified pressure. This pressure is generally controlled by the gas in the apparatus other than the vapor, so that the boiling point is the temperature at which the vapor overcomes the pressure of the residual gas. Below this temperature no distillation occurs; above it, distillation is vigorous.

Under molecular conditions there is by definition no foreign gas, and distillation takes place whenever there is a difference of temperature between the distilland and the condenser. Increase in the absolute temperature and in the temperature difference increases the rate of distillation, but there is no abrupt transition such as boiling available for observation and record. Direct measurements of the rates of distillation are applicable chiefly to pure compounds and afford little information concerning mixtures of dissolved substances.

Fortunately, it is possible to "systematize" the course of molecular distillation so that a property of the constituents of the distilland, analogous to a boiling point, can be measured and used for identification purposes. This can be done most easily for a type of distillation which has reached a position of some importance - the elimination of small quantities of substances such as dyes or vitamins from a large bulk of less volatile fluid, generally an oil.

The method employed depends on two simple postulates: (1) it is assumed that the trace of impurity (potent material) has no affinity for the solvent and (2) that it does not become preferentially located in or excluded from the distilling surface. It then follows that the quantity of potent material evaporated at any moment will be proportional to its mole concentration in the bulk of the distilland.

Two kinds of "rate of distillation" may be defined. The first is the intrinsic rate of distillation, or the "distillability" previously termed the ratio of the number of molecules of a given species leaving the distilling surface in any small interval compared with the number of similar molecules remaining undistilled in the surface layer during the same interval. The second is the rate of elimination or the rate at which the material appears in the receiver. In the distillation of a substance at constant temperature, the distillability will remain constant with the lapse in time. The rate of distillation will decrease exponentially, approaching zero when nearly all the potent material has been evolved.

In order to hasten the elimination of the potent material, it is usually customary to raise the temperature as distillation proceeds. The distillability then increases progressively, but the rate of elimination, which at first rises in like manner, soon falls off to nearly zero because substantially all of the potent material has evaporated.

The Elimination Curve. Much can be learned from molecular distillation by this latter method. A mixture is exposed for distillation for a certain time at each of a series of temperatures, and the amount present of the substance being considered is measured in each fraction(32). These yields, plotted against the temperatures at which the fraction had been distilled, provide a distillation curve which Hickman(40) has called the "elimination curve". This type of curve has the general form shown in Figure 1, page 47.

The amounts of the substance in each fraction increase as the temperature increases until the yields finally reach a maximum and then decrease rapidly to zero because the supply of the substance in the distilland becomes nearly exhausted(32). The elimination curve has an easily recognized shape and a maximum which can be located to within a few degrees.

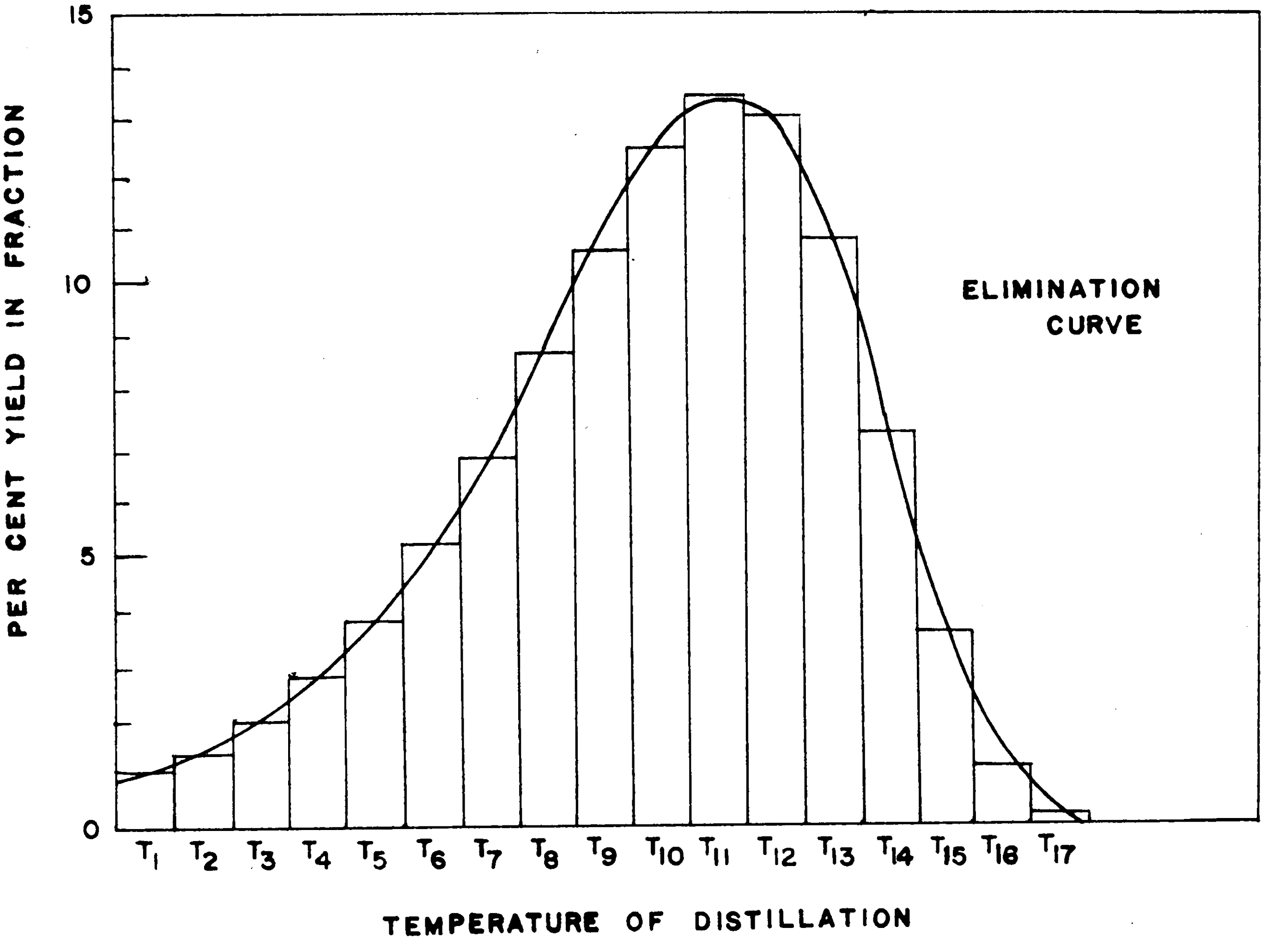

FIGURE I. YIELD VS. TEMPERATURE CHART AND ELIMINATION CURVE

EMBREE, N.D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. **29**, 975 (1937).

The exact shape of the elimination curve and the location of the elimination maximum is determined by the exact procedure employed in the distillation$^{(42)}$. For example, if the distilland is exposed at equal time intervals at each temperature and if the temperature is raised so that the distillability is increased by an equal factor at each step, a curve similar to Curve A, Figure 2, page 49, will be obtained. Embree$^{(33)}$ has shown that this same type of curve can be closely approximated by calculus, Curve B, Figure 2.

The elimination curve is significant in that its shape is independent, within the limits of previous assumptions, of the kind of substance distilled$^{(42)}$. It is the result of a standardized technique applied to the operation of the still during the distillation of any kind of molecule. If an experimental curve has a shape differing from the normal it may be indicative of (1) faulty distillation, Curve D, Figure 2, (2) a substance not obeying the assumptions, or (3) a mixture of substances answering one identifying test.

Thus the shape and position of the elimination curve may be used to reveal many of the properties of a substance and the kind of treatment it has received. A further study of the effects of several operational variables is valuable in consideration of the use of the elimination curve.

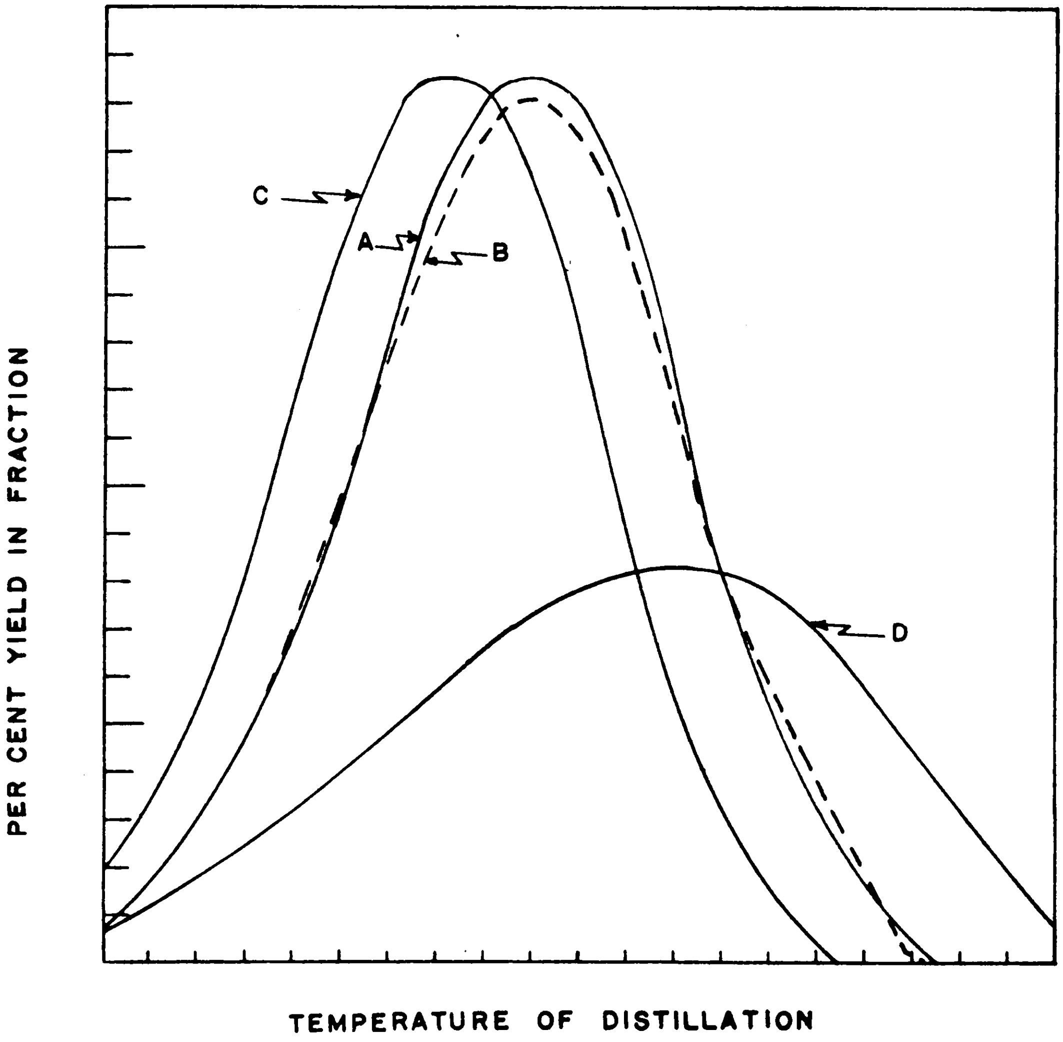

FIGURE 2. ELIMINATION CURVE

A. EXPERIMENTAL VALUES
B. EVALUATED BY CALCULUS
C. TIME INCREMENTS TWICE THAT OF "A"
D. FAULTY DISTILLATION – POOR SURFACE RENEWAL

HICKMAN, K.C.D.: APPARATUS AND METHODS, IND. ENG. CHEM. 29, 971 (1937).

Effect of Distillation Time. The position of the elimination curve is greatly affected by the length of time during which the substance distills at each temperature in the series(34). Figure 3, page 51, shows elimination curves determined for the same substance with distillation times of 1, 2, and 4 minutes at each temperature. The curves show that increasing the time of distillation shifts the maximum of the elimination curve to lower temperatures.

Effect of Initial Temperature. The temperature at which the elimination maximum occurs is a definite property of the substance, if the distillations are always carried out so that the material is distilled for the standard length of time at a temperature series so chosen that the distillability increases by the same factor at each higher temperature(33). The temperature at which distillation is started has no effect on the temperature of the elimination maximum but raises the relative yields at the various temperatures as shown in Figure 4, page 52.

Effect of Heat of Vaporization. Distillability is almost proportional to the vapor pressure(34). Hence, for substances with a high heat of vaporization, the distillability will increase rapidly with temperature, and the elimination curve will be narrow and steep in comparison with substances with a

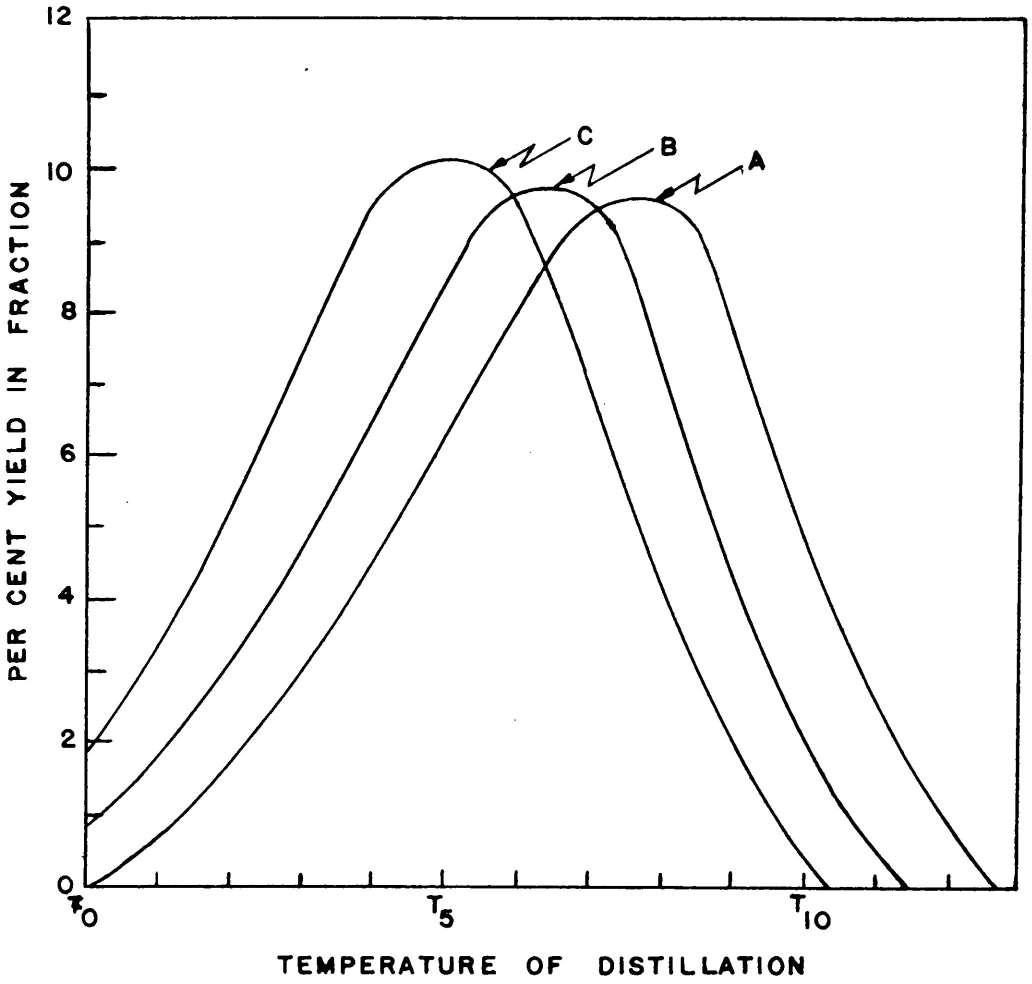

FIGURE 3. EFFECT OF TIME OF DISTILLATION ON ELIMINATION CURVES

A. DISTILLATION FOR 1 MINUTE AT EACH TEMPERATURE.
B. DISTILLATION FOR 2 MINUTES AT EACH TEMPERATURE.
C. DISTILLATION FOR 4 MINUTES AT EACH TEMPERATURE.

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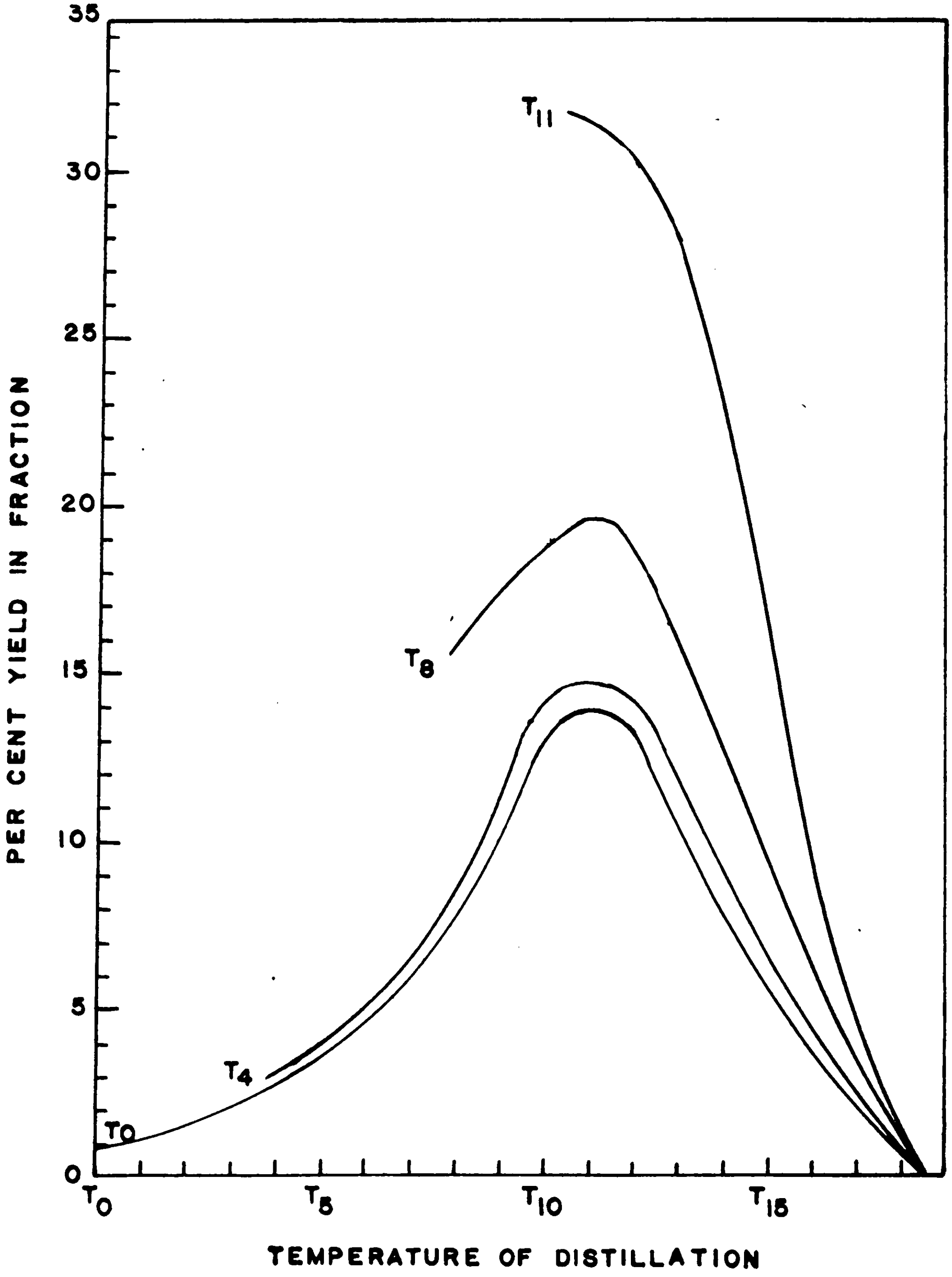

FIGURE 4. EFFECT OF INITIAL TEMPERATURE ON ELIMINATION CURVES

EMBREE, N. D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 978 (1937).

low heat of vaporization which have broader and flatter elimination curves. Typical curves for two substances, one with a high and the other with a low heat of vaporization, are shown in Figure 5, page 54.

Effect of Solvent Distilling Over with Potent Material. In many distillations, it is desirable to have a small amount of the solvent distilling over with each fraction to aid in drainage or washing of the distillate from the condenser surface(34). Figure 6, page 55, shows the typical difference in the elimination curves when two per cent of the total solvent distilled over with the potent material in each fraction.

Effect of Use of an Arithmetic Series of Temperatures. If the distillation is carried out at an arithmetic series of temperatures instead of a series chosen so that the distillability increases by a constant factor at each temperature, the elimination curve will have a somewhat different shape(34) as shown in Figure 6, page 55.

Effect of Continuous Distillability Change. In some cases it might be desirable to have the distillability increase continuously instead of by increments. This condition might exist when a still is being supplied with a greater amount of energy than is necessary to maintain a constant temperature

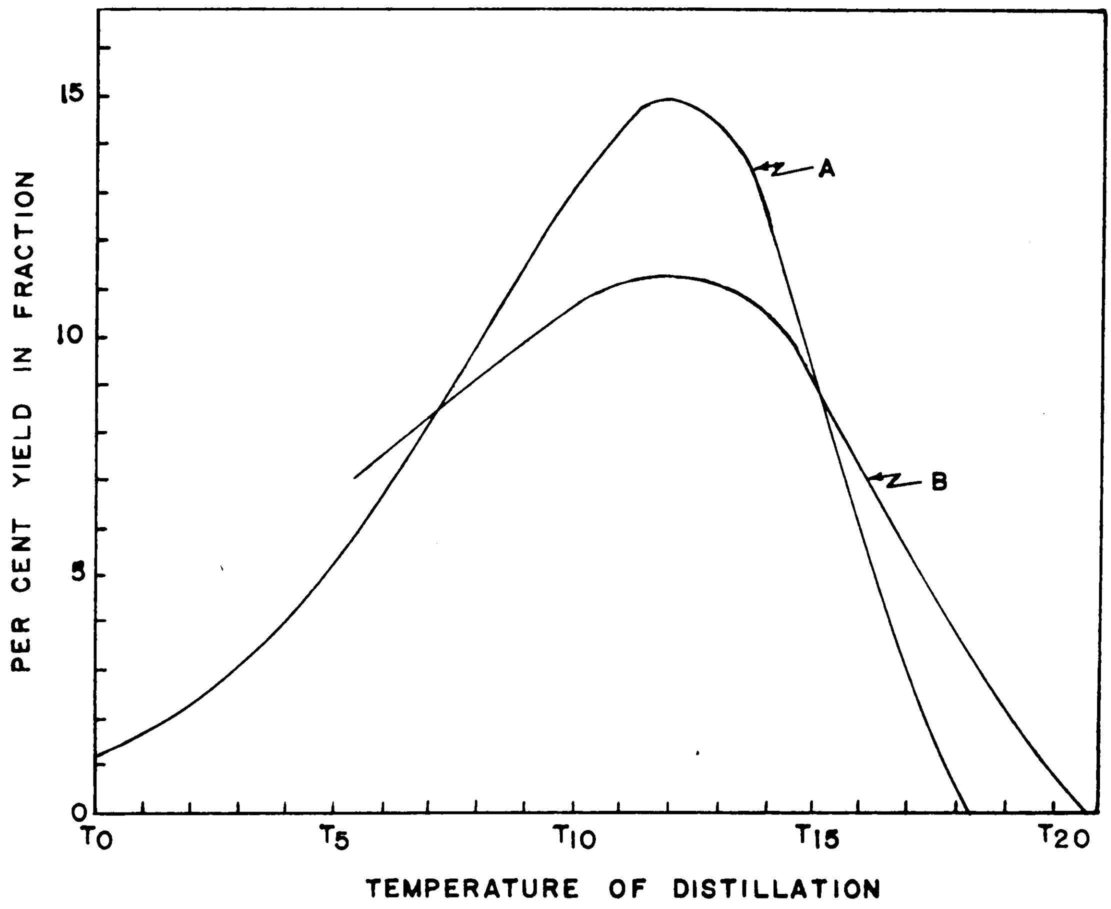

FIGURE 5. EFFECT OF HEAT OF VAPORIZATION ON ELIMINATION CURVES

A. SUBSTANCE WITH HIGH HEAT OF VAPORIZATION.

B. SUBSTANCE WITH LOW HEAT OF VAPORIZATION.

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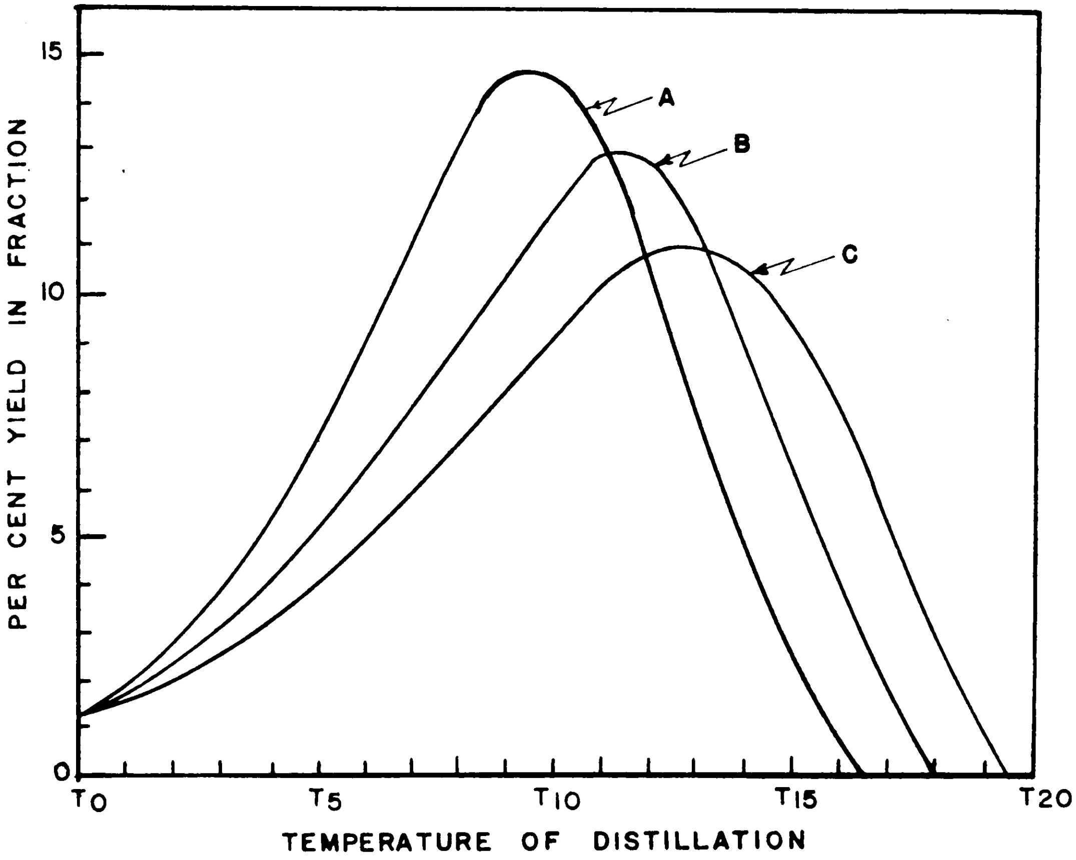


FIGURE 6. ELIMINATION CURVES FOR VARIOUS CONDITIONS

A. TWO PER CENT OF SOLVENT DISTILLING IN EACH FRACTION.
B. NO SOLVENT DISTILLING WITH POTENT MATERIALS.
C. DISTILLATION WITH AN ARITHMETIC SERIES OF TEMPERATURES.

EMBREE, N. D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 979 (1937).

or if the distilland is allowed to flow as a column that is heated at the bottom. If the distillability is increased continuously for one minute distillation increments, a curve similar to Curve A, Figure 7, page 57, might be obtained. If the temperature is increased more slowly, for instance, 2 or 4 minute periods, Curves B or C result. The shifting of the temperature of the maximum to a lower value is similar to that encountered by merely increasing the distillation time for constant temperature (constant distillability) increments as shown in Figure 3, page 51.

The Elimination Maximum. Under standardized conditions of molecular distillation, the elimination curve of any individual substance depends on its distillability. Under such conditions, the position of the maximum is reproducible with a precision of one degree Centigrade. Hickman(43) suggests that "this position is as valuable an attribute of a substance as the boiling point would be if it could be determined at a higher pressure".

Any group of substances can be arranged with the distillabilities in serial order when the conditions of distillation are standardized(43). The elimination maximum will occur for each substance in a fixed relative order with definite temperature intervals between the maxima. Changing the conditions will then shift all the maxima up or down the temperature scale but will

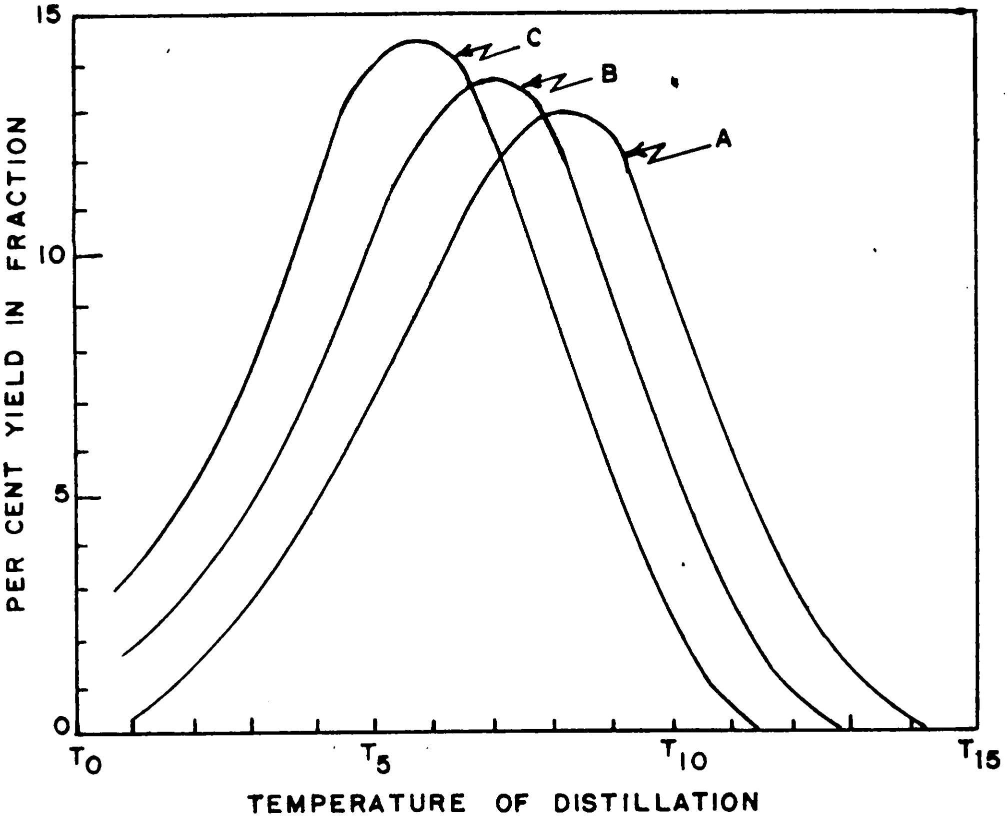


FIGURE 7. ELIMINATION CURVES FOR CONTINUOUS DISTILLABILITY CHANGE

A. DISTILLATION FOR 1 MINUTE AT EACH TEMPERATURE.
B. DISTILLATION FOR 2 MINUTES AT EACH TEMPERATURE.
C. DISTILLATION FOR 4 MINUTES AT EACH TEMPERATURE.

EMBREE, N. D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 979 (1937).

not seriously alter the separation or the relative order except between substances of widely different latent heats. This important aspect of molecular distillation enables the investigator to use certain dyes as distillation pilots which are readily detected and estimated.

Pilot Dyes. Pilot dyes(45) are probably most useful in assisting in the isolation of an unknown substance or in studying the action of new apparatus. In the study of an unknown substance, the approximate shape and position of the elimination curve of the substance is first determined. The choice of an appropriate pilot dye or dyes can be made which will allow an estimation of the concentration of the unknown substance in a particular fraction from the color of the dye in the fraction when the dye or dyes are distilled with the unknown substance. Checks on the unknown substance need be made only rarely by test or biological assay which results in a great time saving during the study of the distillation of the unknown substance.

As for studying the action of new apparatus, pilot dyes with their ease of analysis by colorimetric methods, permit relatively easy studies on the distillation characteristics of a newly designed still and on the operation variables of the still.

Several anthraquinone dyes often used as pilot dyes and their approximate elimination maxima are given in Figure 8, page 59.

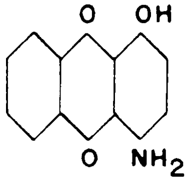
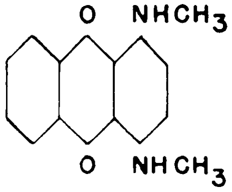
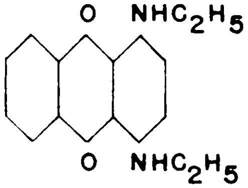
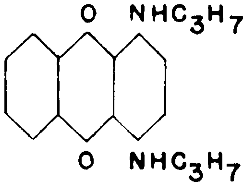
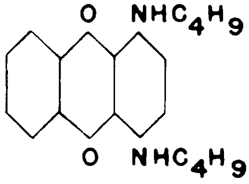
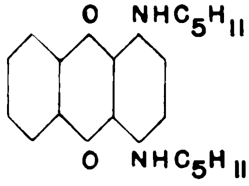
NAME	FORMULA	RELATIVE ELIMINATION MAXIMUM °C
CELANTHRENE RED 3B		127
DIMETHYLDIAMINO-ANTHRAQUINONE		141
DIETHYLDIAMINO-ANTHRAQUINONE		153
DIPROPYLDIAMINO-ANTHRAQUINONE		162
DIBUTYLDIAMINO-ANTHRAQUINONE		171
DIAMYLDIAMINO-ANTHRAQUINONE		183

FIGURE 8. APPROXIMATE MAXIMA OF PILOT DYES

HICKMAN, K. C. D.: APPARATUS AND METHODS, IND. ENG. CHEM., 29, 978 (1937).

Composite Elimination Curves. When a mixture of two or more potent materials is distilled, entirely abnormal shaped curves are often encountered(45). The mixture is generally very difficult to resolve. It is necessary to apply repeated fractionations by ordinary molecular distillation and then to compare the elimination curves from the distillation of the extreme fractions. The probable resolution of binary mixtures has been studied by Hickman(45) by constructing composite curves representing the addition to one substance, quantities varying from 1/4 to 4 times the quantities of the second substance. The elimination maxima of the two substances varied by 5, 10, 20, and 40 degrees Centigrade. Figure 9, page 61, shows the composite curves for the variations. Hickman suggests the second substance can be detected if present in 1/2 the quantity or more and boiling at least 10 degrees from the main constituent. When smaller quantities of nearer distilling materials are present, the only effect often is to shift the position of the maximum to a false location. The remedy is to fractionate the parent material and secure curves for the head and tail fractions of the primary elimination curve.

Constant-Yield Oil. It has previously been stated that it is often desirable for a small portion of the solvent to distill with the potent material in each fraction to provide for drainage of the distillate from the condenser. This is absolutely necessary in

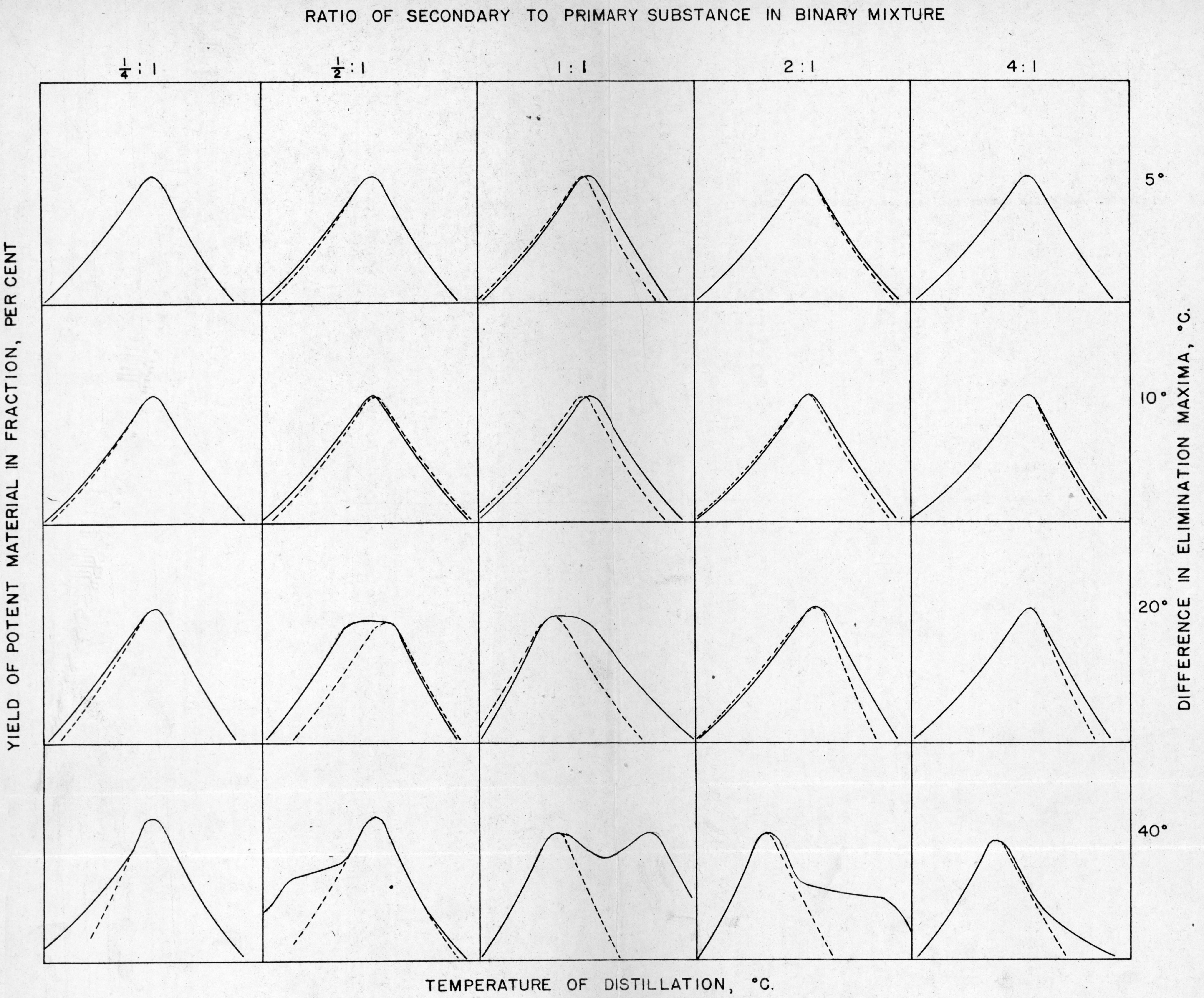


FIGURE 9. COMPOSITE CURVES FOR VARIOUS TYPICAL COMPOUNDS

HICKMAN, K.C.D.: APPARATUS AND METHODS, IND. ENG. CHEM., 29, 974 (1937).

many cases where distillations are carried out to identify rather than separate a constituent(44). In these instances, it is imperative that the drainage error be kept uniform. When only small traces of the potent material are distilled during a temperature increment, the material may collect as a mist on the condenser which will not drain adequately and the result is large error in the elimination curve of that substance.

The potent material should therefore be dispersed in a medium which yields a similar volume of distillate for each succeeding temperature interval to keep the drainage uniform(44). The volume of distilland should not be reduced by more than half by the end of distillation, however.

Since it is not the nature of most oils to distill at a constant rate over even small temperature ranges, it is usually necessary to prepare a constant-yield oil by blending equal fractions of oil obtained from numerous repeated molecular distillations. Constant-yield oils (CYO) have been prepared by blending various nonreactive solvents, such as heavy petroleum fractions. Baxter et al(2) have described in detail one such oil, a pure triglyceride or mixture of glycerides. The yields of the various fractions obtained from the distillation of such a constant-yield oil are presented in Table IV, page 63.

TABLE IV

Data on Constant-Yield Mixture T-175

Fraction	Temperature	Residual Gas Pressure	Weight
	°C	mm x 10^3	gm
1	100	1.4	2.2
2	110	1.3	1.9
3	120	1.2	2.5
4	130	1.2	2.9
5	140	1.2	3.3
6	150	1.3	3.8
7	160	1.5	4.0
8	170	1.7	3.5
9	180	1.8	3.0
10	190	2.0	2.9
11	200	1.9	3.1
12	210	1.8	3.5
13	220	1.4	3.6
14	230	1.2	4.5
15	240	1.2	5.7
16	250	1.2	7.3

Baxter, J. G., E. LeB. Gray, and A. O. Tischer: Preparation and Characteristics of Synthetic Constant-Yield Mixtures, Ind. and Eng. Chem., 29, 977 (1937).

III. EXPERIMENTAL

The purpose of this investigation, the plan of experimentation, the materials and apparatus used, the method of procedure followed, and the data and results obtained in the investigation are presented.

Purpose of Investigation

The purpose of this investigation was the determination of the single and composite elimination curves from the molecular distillation of several anthraquinone dyes dispersed in a mineral constant-yield oil and the attempted separation of binary mixtures of dyes by various redistillative techniques.

Plan of Experimentation

The plan followed in the investigation consisted of a literature review, the design and construction of an all-metal molecular still, preliminary tests made on the equipment, operational tests, and analysis of results.

Literature Review. A survey of all available literature pertaining to high-vacuum distillation and particularly to molecular distillation was made to gain an insight into the work which had been done by previous investigators. Particular attention was focused on the literature which dealt with analytical distillation of pilot dyes as well as on the technique employed by the various investigators.

Design and Construction of an All-Metal Molecular Still. An all-metal molecular still to replace the glass still used by Coli was designed to incorporate the recommendations made by Coli(28). The new unit was constructed using copper as the basic material of construction. Many modifications to the original design were incorporated into the unit whenever the equipment failed to operate as desired or when operation was simplified by change in equipment.

Preliminary Tests. Numerous preliminary tests were made on the entire unit and on the various component parts to determine such items as the flow characteristics of the feed oil through the system and the vacuum techniques to be employed during the actual operational tests.

Experimental Tests. Initial tests were made in an effort to obtain a constant-yield oil for use as the dye solvent and to standardize an operational technique for the experimental tests. The elimination curves for the molecular distillation of various single anthraquinone dyes were obtained under standardized operating conditions. Composite curves for various binary mixtures and a tertiary mixture of dyes were determined. Molecular redistillation of binary mixtures of anthraquinone dyes was performed to study the separatory ability of the laboratory molecular still.

Analysis of Results. The data obtained and the results of the investigation were discussed primarily to evaluate the experimental work performed. Special emphasis was given to the distillation of binary mixtures and to the use of the molecular still to separate such mixtures. Recommendations for future studies and for modifications in still design to improve operation were presented.

Materials

The following materials were used in this investigation:

Benzene. Purified, code No 1444, lot No G-100-J. Obtained from Allied Chemical and Dye Corporation, General Chemical Division, New York, N. Y. Used to rinse all glassware used in connection with preparing and testing the various oil fractions.

Carbon. Decolorizing, code No 1551, lot No E297. Obtained from Allied Chemical and Dye Corporation, General Chemical Division, New York, N. Y. Used in tests attempting to decolorize Esso motor oil for preparation of a constant-yield oil.

Dyes. The following anthraquinone dyes were used in the investigation:

Celanthrene Red 3B. Concentrated 125 %, code No W-258, chemical formula, $C_{14}H_9O_3N$. Obtained through courtesy E. I. du Pont de Nemours and Company, Organic Chemicals Department, Dyestuffs Division, Wilmington, Delaware. Letter dated December 2, 1952.

2,6-Dimethyldiaminoanthraquinone. Code No MDD-3075, chemical formula, $C_{16}H_{14}O_2N_2$. Obtained through courtesy E. I. du Pont de Nemours and Company, Organic Chemicals Department, Dyestuffs Division, Wilmington, Delaware. Letter dated December 2, 1952.

1,4-Diethyldiaminoanthraquinone. Code No R-2135-60-B, chemical formula, $C_{18}H_{18}O_2 N_2$. Obtained through courtesy American Cyanamid Company, Calco Chemical Division, Bound Brook, New Jersey. Letter dated December 1, 1952.

1,4-Diisopropyldiaminoanthraquinone. Code No MMD-3077, chemical formula, $C_{20}H_{22}O_2N_2$. Obtained through courtesy E. I. du Pont de Nemours and Company, Organic Chemicals Department, Dyestuffs Division, Wilmington, Delaware. Letter dated December 2, 1952.

1,4-Dibutyldiaminoanthraquinone. Code No R-2135-60-G, chemical formula, $C_{22}H_{26}O_2N_2$. Obtained through courtesy American Cyanamid Company, Calco Chemical Division, Bound Brook, New Jersey. Letter dated December 1, 1952.

Flux. Meets specifications U.S. N. 51F4A, Army Air Corps No 11316A, and Army Ordnance Department No AXS-500. Manufactured by Handy and Harman, Inc., New York, N. Y. Used as flux for silver soldering of copper tubing-fitting connections.

Grease. High-vacuum, celvacene heavy, lot No 665. Manufactured by Consolidated Vacuum Corporation (formerly Distillation Products Industries), Rochester, N. Y. Used in testing for leaks around fittings and tanks in assembled still.

Grease. Andok *B*, lubricant. Manufactured by Esso Standard Oil Company, Baton Rouge, La. Used as lubricant for rotor shaft.

Ice. Made in home refrigerator. Used in thermos bottles for thermocouple cold junction.

Oil. Mineral, colorless, light and heavy grades, light oil boiling range 330 to 360 °C; heavy oil boiling range, 360 to 390 °C. Manufacturer unknown. Obtained from Tech Drug Store, Blacksburg, Virginia. Used as component of feed mixture as carrier for dyes.

Oil. Mineral, colorless, extra heavy grade. Obtained through courtesy Esso Standard Oil Company, Linden, N. J. Used as component of feed mixture as carrier for dyes.

Oil. Amoil-S, stock No 8114. Obtained from Consolidated Vacuum Corporation (formerly Distillation Products Industries), Rochester, N. Y. Used as working fluid in diffusion pumps.

Oil. Cenco, hyvac, No 93050C. Obtained from Central Scientific Company, Chicago, Illinois. Used as lubricant and sealing fluid in Cenco hyvac and megavac forepumps.

Oil. Kerosene. Obtained from Texas Oil Company, Christiansburg, Virginia. Used for flushing still between tests.

Oil. Essolube No 7. Obtained from Esso Standard Oil Company, Christiansburg, Virginia. Used in decolorizing tests as a possible component for a constant-yield oil.

Packing. Garlock 926, Plastallic, consists of asbestos fiber, shreds of lead, graphite, and heat resistant lubricant. Supplied by Comas Cigarette Machine Company, Salem, Virginia. Used as packing around the rotor shaft in housing.

Packing. Plastic Metallic, style 10. Obtained from the Hollow Center Packing Company, Cleveland, Ohio. Used for packing the rotor shaft in housing.

Packing. Valley Forge, valve stem, braided, 3/8-inch, style No A-25. Obtained from Noland Company, Roanoke, Virginia. Used for packing the rotor shaft in housing.

Packing. Crane, water pump, lead-covered fiber, 1/4-inch, style No 112. Manufactured by Crane Packing Company, Chicago, Illinois. Used for packing the rotor shaft in housing.

Sealit. Fisher, catalog No 4-762. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in testing for leaks in assembly of still.

Solder. Sil-fos, 15 % silver content alloy, starts to melt at 1185 °F and is completely liquid at 1300 °F. Distributed by Southern Oxygen Company, Roanoke, Virginia. Used in welding numerous connections in the construction of the still.

Valve Grinding Compound. Clover brand, grades E and A. Manufactured by the Clover Manufacturing Company, Norwalk, Conn. Used in preliminary grinding of the bell jar to base plate of still to form vacuum-tight seal.

Vaseline. White petroleum jelly. Manufactured by Chesebrough Manufacturing Company, New York, N. Y. Used in attempts to make a high-boiling range constant yield oil.

Wax. Paraffin, household grade. Manufactured by Esso Standard Oil Company, Linden, N. J. Used in attempts to make a high-boiling range constant yield oil.

Apparatus

The following apparatus and equipment were used in the course of this investigation:

Balance. Analytical, Seeder-Kohlbusch with chainweight and magnetic damping attachments, capacity 200 grams each pan, sensitivity 1/20 milligram. Obtained from Phipps and Bird, Inc., Richmond, Virginia. Used to weigh dye samples in feed preparation.

Bottles. Specimen, with black molded plastic screw caps, catalog No 3-338, sizes H and L. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used as sample containers for distillate fractions.

Blender. Waring, catalog No 14-509-10, 115 v, 60 cy, ac, 10,000 rpm. Container, 1000-ml capacity, provided with bakelite splash cover. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to disperse dye in constant-yield oil in preparing distilland mixtures.

Cell. Dry, No 6, 1-1/2 v. Manufactured by the National Carbon Company, Cleveland, Ohio. Used in conjunction with potentiometer for temperature measurements.

Cell. Standard, Eppley, student, cadmium, unsaturated, catalog No 11-506-38. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used for zero balancing of potentiometer.

Colorimeter. Klett, photoelectric, type 7093, 115 v, 60 cy, ac. Obtained from Klett Manufacturing Company, New York, N. Y. Used to analyze feed and product samples colorimetrically.

Counter. Veeder, range 0 to 9999. Obtained from Fisher Scientific Company, Pittsburgh, Pa. Used to determine speed of rotor.

Feed Pump. Drawing 1, page 91 shows the assembled feed pump with component parts identified:

Balls. Brass, 5/16-inch diameter. Obtained from Blacksburg Motor Company, Blacksburg, Virginia. Used as check in conjunction with piston and check valve at top of pump.

Body. The body of the pump was made from a 7-inch length of 3/4-inch outside diameter copper tubing. The internal diameter was machined to 0.5500 inch. The top check valve seat, E, was pressed into the body a distance of 3/8 inch. A 1-inch length of the 3/4-inch tubing, to which a 1/4-inch exit line had been welded was slipped over the portion of the ball check valve protruding from the body. The ends of the two pieces of 3/4-inch tubing were brought firmly together and soldered into place. A spring stop, F, was placed on the bottom end of the pump in a similar manner. This method of construction allows for disassembly of the pump and access to all parts by merely melting the soft-soldered joints. A 2-inch length of 1/4-inch copper tubing, to serve as inlet , was welded to the body near the bottom so that the center-line through the tubing would be at the bottom of the piston when the pump was assembled as shown in the diagram. The body was made in the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia.

Piston. Steel, round stock, 0.5300 inch outside diameter, 1-3/8 inches long with 1/4-inch hole bored on center and traversing its length. The stock was countersunk 41 degrees on one end sufficiently deep to form a seat for a 5/16-inch brass ball. Clearance between piston and pump wall was 0.0100 inch. Machining of the piston was done in Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as the piston in the feed pump.

Spring. Five-sixteenths inch diameter coil, 1 inch long, 0.020 inch diameter wire. Obtained from Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to return piston to normal position during pumping operation.

Feed Pump Power Supply. Drawing 4, page 100 shows the wiring diagram of the power supply of the field coil for the feed pump described above. The component parts are described below:

Chassis. Formerly used as chassis for an aircraft IFF set. Manufacturer unknown. Obtained from war surplus. Used as chassis for feed pump power supply.

Dynamotor. Number R33621, type sp-175, s.s. 2867, 4000 rpm. Manufactured by Pioneer Gen-E-Motor, Chicago, Illinois. Obtained from war surplus. Rewired(17) and used as a direct current motor to regulate pumping speed of feed pump.

Field Coil. Bore, 5/8-inch. Manufacturer unknown. Obtained from a 5-inch speaker of small radio. Used to actuate piston of feed pump.

Resistor. IRC type EP, 1000 ohms. Obtained from Leonard Electronic Supply Company, Roanoke, Virginia. Used to decrease current to field coil.

Transformer. Thordarson, filiment type T92R21, 110 v to 5 v. Obtained from Allied Radio Corporation, Chicago, Illinois. Used in conjunction with rectifying tube.

Vacuum Tube. Full wave rectifier tube, RCA, type 5T4. Manufactured by Radio Corporation of America, New York, N. Y. Used to supply direct current to field coil.

Feed Pump. Hills-McCanna proportionating, type UM-1F, serial No 13137, single acting, body, steel; gland, steel; plunger, 1/2-inch porcelain; packing, crane No 810-S; check valves, 1/4-inch double cone type, stroke adjustment, stationary micro screw; speed, 30 spm; maximum capacity, 1.62 gph; minimum capacity, 0.16 gph; maximum pressure, 500 psi, gage; suction lift, 10 feet of water; maximum length of stroke, 1-1/4 inches. Pump equipped with a 1/4 hp, 110 v, 1 ph, 60 cy, 1725 rpm, group D explosion proof, G. E. motor. Obtained from Hills-McCanna Company, Chicago, Ill. Used in the preliminary reconstruction of the all-metal, molecular still assembly as the feed pump.

Feed and Product System. Drawing 2, page 92 shows the feed and product system used in the investigation. The component parts of this system are:

Heater Element. Thermalink, model No 42T2C2, 0.281 inch outside diameter, flexible copper sheath, 230 v, ac, 1750 w. Obtained from Electro-Therm Incorporated, Silver Spring, Maryland. Used as auxiliary heater to preheat the feed.

Fittings. Swagelok, brass, assorted tees, adapters, and valves for 1/4-inch copper tubing. Manufactured by Crawford Fitting Company, Cleveland, Ohio. Used in connecting copper flow lines in still assembly.

Tank, Loading. Copper, cylindrical, 1-1/2 inches outside diameter by 3 inches high, open at one end, concave bottom with 1/4-inch tubing welded to center for drain. Constructed in the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as feed loading tank.

Tanks, Feed, Residue. Copper, cylindrical, 4 inches outside diameter by 4 inches high, both ends closed, top flat, bottoms concaved for drainage, all joints and connections, silver-soldered. See items T and S, Drawing 2, page 92. Constructed in the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Tank S used as primary feed tank and tank T used in conjunction with calibration of feed pump.

Tank, Distillate. Copper, cylindrical, 3 inches outside diameter by 6 inches high, closed at both ends, necessary connections for venting, evacuation, entry and discharge of product. Constructed in the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as collecting tank for distillate product.

Tape, Heating. Electrothermal, 130 v, ac, 3.8 amp maximum. Made in England. Obtained from E. Machlett and Son, New York, N. Y. Used for preliminary heating of feed and distillate tanks and distillate-product drawoff line.

Tubing. Copper, 1/4-inch. Manufactured by National Copper and Smelting Company, Cleveland, Ohio. Used for all flow, vacuum, and vent lines in feed and product system.

Flask. Distilling, pyrex, three-neck, one-liter capacity. Manufactured by Corning Glass Company, Corning, N. Y. Used as oil-bath container in thermocouple calibration.

Galvanometer. Pointer type, DC, catalog No 11-506-27, model B with scale of 60 divisions of 1 millimeter each, sensitivity, 0.20 microampere per millimeter. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used with potentiometer for temperature determinations of feed and residue using the respective thermocouples.

Gage. McLeod, vacuum, type MG-07, triple range, table model, pump operated, range 0 to 5000 microns. Manufactured by and obtained from Consolidated Vacuum Corporation (formerly Distillation Products Industries), Rochester, N. Y. Used to measure the pressure in the molecular still.

Glassware. Assorted pyrex glassware such as beakers of various sizes, pipets, erlenmeyer flasks, graduated cylinders, funnels. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in feed and dye standards preparation and in sampling.

Heater. Glas-col, serial No 99875, 110 v, ac. Manufactured by the Glas-col Apparatus Company, Terre Haute, Indiana. Used to heat distilling flask containing oil for thermocouple calibration.

Hot Plate. Fisher autemp, catalog No 11-467-1, model A for 115 v, ac. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in decolorizing experiments of Essolube No 7 motor oil and to preheat feed before adding it to feed tank of molecular still.

Instrument Panel. The following items are mounted on the instrument panel of the still. See Drawing 4, page 100.

Autotransformers. Powerstat, type 116, 115 v, 60 cy, ac, 1 KVA maximum. Manufactured by Superior Electric Company, Bristol, Conn. One powerstat used to control rotor heater temperature; one to control feed tank heater temperature; and one used to control distillate product line and tank heater temperature.

Autotransformer. Amertran, voltage regulator, catalog No 1H-11B, serial No 7031561, 230 v, ac, 11 amp maximum. Manufactured by American Transformer Company, Newark, N. J. Used to control temperature of feed preheater element.

Circuit Breaker. Capacity, 15 amperes. Manufactured by General Electric Company, Bridgeport, Conn. Used to limit total current flow to instrument panel.

Pilot Lights. One hundred ten volt alternating current. Obtained from war surplus. Used in various circuits on instrument panel.

Resistor. Variable, IRC type PR-25, 25 w, 5000 ohm, dial type. Obtained from Leonard Electronic Supply Company, Roanoke, Virginia. Used to control number of strokes per unit time of feed pump.

Switches. Single-pole, single-throw, toggle. Obtained from war surplus. Used to control current flow in various circuits.

Motor. Electric, single phase, 115 v, 60 cy, ac, 1/4 hp, 1725 rpm, 40 °C temperature rise. Obtained from Westinghouse Electric Corporation, Bluefield, West Virginia. Used to rotate rotor of still.

Potentiometer. Fisher, type S, catalog No 11-506-1, two ranges, 0 to 0.017 v and 0 to 1.70 v. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to measure voltage across thermocouples for indication of feed and residue temperatures.

Still Head Assembly. Drawing 6, page 101, shows as assembly drawing of the still head. The component parts of the assembly are described as follows:

Base Plate. Shown as item B, steel, 15 inch diameter, 3/4-inch thick, drilled to accommodate vacuum outlet, feed inlet, distillate outlet, residue outlet, rotor heater leads (spark plugs), vacuum gage inlet line, and residue thermocouple inlet line; circular groove 7-7/8 inches I. D. x 9 inches O. D. x 1/4-inch deep cut into face of plate to accommodate silicone gasket for seal between bell jar and base plate. Original plate fabricated by Comas Cigarette Machine Company, Salem, Virginia. Modifications made in Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia.

Bearing Housing. Shown in Drawing 7, page 111, steel, 1-1/2 inches O. D. x 8-1/4 inches long, drilled to accommodate bearing for 1/2-inch shaft. Bearing surface consisted of one 1/2-inch oilyte bearing 1-1/4 inches long press fitted into front end of bearing housing, 3 inches of Plastallic packing, 3-1/2 inch lantern ring for lubrication purposes, and a 1-1/2 inch self-centering floating head bearing in tightening nut. A 1/4-inch pipe nipple 2 inches long with grease cup attached was welded to housing 1-3/4 inches from back end. Constructed in the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to contain bearings and packing for vacuum seal of rotor shaft.

Bearing Mount. Cast iron, longitudinal section machined from housing section of mount to accommodate the grease fitting that was welded to rotor-shaft housing to allow for easy assembly and disassembly of base plate-rotor assembly from still set-up. Obtained from Comas Cigarette Machine Company, Salem, Virginia. Machining of section done in the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to secure base plate-rotor assembly into position.

Bell Jar. Pyrex, low form, 4-3/4 inches high by 8 inches inside diameter. Obtained from Fisher Scientific Company, New York, N. Y. Used to enclose rotor and to serve as condenser in still-head assembly.

Collecting Gutter. See item E, Drawing 5, page 101. Rolled bronze; gutter constructed to fit around the periphery of the rotor with a clearance of 1/32-inch; outside diameter of gutter is 5-3/4 inches; inside diameter is 4-1/4 inches; thickness is 3/4 inch. Soldered to the back of the gutter is a 3/4-inch copper sleeve, 4-3/4 inches in diameter with a 1/4-inch lip to catch any dripping or overflow from the gutter. There is a 5/16-inch copper tubing outlet on the outer edge of the gutter and a corresponding outlet on the sleeve extension. Both outlets enter a common header that serves as the residue draw-off line. Fabricated by the Comas Cigarette Machine Company, Salem, Virginia. Used to collect the residue, or undistilled portion of the feed mixture as it is thrown from the edge of the rotor in a fine spray.

Gasket. Silastic, No 7-170, silicone rubber, 7-7/8 inches I. D. x 9 inches O. D. x 1/8-inch thick. Obtained from Dow-Corning Corporation, Midland, Michigan. Used for seal between bell jar and base plate of still.

Heater. Chromalox ring element, catalog No A-20, type A, 115 v, 60 cy, ac, 300 w, chrome steel sheath, single heat, for temperatures up to 1200 °F maximum. Obtained from Edwin L. Wiegand Company, Pittsburgh, Pa. Used as heater for rotor.

Lantern Ring. Brass, shown as item H, Drawing 7, page 111. Overall length, 3-3/4 inches; outside diameter, 1 inch for distance of 3/8 inch from each end, then outside diameter is decreased to 7/8 inch to allow for grease flow along length of ring. Four rows of five 1/8-inch diameter holes drilled equidistant along length of small diameter of ring 90 degrees apart to allow grease to flow on to shaft. On inside surface of the ring, beneath each hole, a semi-circular groove 1/8-inch wide and 1/16-inch deep was cut to insure grease shaft contact and a vacuum tight seal while the shaft was rotating. Both ends of ring were countersunk 45 degrees to direct packing against the shaft. Machined in Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used for lubrication of shaft and to obtain vacuum-tight seal around shaft.

Packing or Tightening Nut. Steel, 2-1/4 inches O. D. x 2-1/4 inches long, threaded to fit housing as shown in Drawing 7, page 111. Brass, self-centering floating head contained within tightening nut as shown by item G, Drawing 7. Machined in the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to tighten and keep packing pressed against rotor shaft.

Rotor. Shown as item A, Drawing 5, page 101, aluminum; outside diameter, 4.11 inches; thickness at outer edge, 2.075 inches; angle of inclination of rotor surface, 52-1/2 degrees, slant height of rotor surface, 2.59 inches. Fabricated by Comas Cigarette Machine Company, Salem, Virginia. Used as the evaporating surface(19).

Rotor Plate and Shaft. Shown as item K, Drawing 5, page 101, steel; diameter of plate, 5 inches; thickness of plate, 1/4 inch; diameter of shaft, 1/2 inch, length of shaft, 13 inches. Plate welded to shaft. Fabricated by Comas Cigarette Machine Company, Salem, Virginia. Used as mount for evaporating surface, the rotor, of the molecular still.

Spark Plugs. AC, No 45; side contacts removed, 1/2-inch length of a No 10 bolt was welded to the center terminal to attach heater leads. Base plate drilled and tapped to accommodate plugs; vacuum-tight seal obtained by tightening plugs down on lead gaskets. Manufactured by General Motors Corporation, Detroit, Michigan. Used to connect heater to electric power source through the base plate.

Still Head Assembly Modified to Enclose Rotor Motor in Vacuum System. Drawing 9, page 119, shows an assembly drawing of the still head and vacuum chamber enclosing rotor drive. The component parts of the modified assembly, not previously described, that were machined and fabricated in the Industrial Engineering Shops, Virginia Polytechnic Institute, Blacksburg, Virginia, are described as follows:

Base Plate. Shown as item E; steel; 12 inches diameter; 5/8-inch thick; drilled to accommodate feed inlet, distillate outlet, and residue outlet on the outer periphery of the plate; a 3-inch hole in the center of the plate to accommodate the rotor shaft; a 3/8-inch hole to accommodate the heater lead attachments; a circular groove 7-7/8 inches I. D. x 9 inches O. D. x 1/8-inch deep machined into face of plate to accommodate a silicone gasket for seal between bell jar and base plate.

Rotor Support and Shaft. Shown as item S; steel; diameter of plate, 5 inches; thickness of plate, 1/4 inch; diameter of shaft, 7/8 inch; length of shaft, 3 inches; shaft drilled to accommodate 1/2-inch motor shaft. Plate threaded to shaft and secured in place by locknut.

Vacuum Housing for Motor Drive for Rotor. Shown as item *H*; standard 8-inch iron pipe; 11-1/2 inches long; secured to back of the plate and to back flange by electric welding; drilled to accommodate residue thermocouple inlet, vacuum outlet to diffusion pump; outlet to McLeod gage, and inlet for cooling water to coils surrounding rotor motor as shown; outlet adapters, steel, to accommodate 1/4-inch copper tubing, secured to housing by bronzing; a circular groove 8-1/4 inches I. D. x 9-1/4 inches O. D. x 1/8-inch deep machined into outer face of back flange to accommodate a silicone gasket for vacuum seal to blank flange.

Blank Flange. Steel; 12-inch diameter; 7/8-inch thick; drilled and tapped to accommodate spark plugs used for rotor heater and drive motor lead attachments to power supply.

Motor. Type ADS, style 957656-B, serial KU, 1/4 hp, 50 °C temperature rise, 115 v, 60 cy, ac, 10,000 rpm, variable speed. Wrapped with 10 feet of 3/16-inch copper tubing for cooling purposes. Manufactured by Westinghouse Electric Corporation, Pittsburgh, Pa. Used as drive for rotor.

Strobotac. Type No 631-B, serial No 10621, 110 v, 60 cy, ac. Manufactured by the General Radio Company, Cambridge, Mass. Used to determine the rotor speed.

Thermocouples. Copper - constantan. Constructed from 3/32-inch copper tubing (serving as copper lead) and insulated Leeds and Northrup No 24 constantan wire. Wire was inserted into tube and beaded at one end forming junction; junction secured and made vacuum tight by fusing the copper and constantan together at the junction. The thermocouples were inserted into the feed and vacuum lines through the run of a copper tubing tee and secured into place by compression fittings around a 1/4-inch collar soldered to the thermocouple tube as shown in Drawing 10, page 128. Constantan wire obtained from Leeds and Northrup Company, Philadelphia, Pa. Used to determine temperatures of feed and residue during tests.

Thermometer. Certified, catalog No 15-040, range -5 to 101 °C in 1/10 °C increments. Obtained from Eimer and Amend, New York, N. Y. Used in calibration of thermocouples.

Thermos Bottle. One pint capacity. Obtained from Brown Stores Company, Blacksburg, Virginia. Used as cold junction for thermocouples.

Transformer. Constant voltage; serial No G2113; primary volts, 95 to 125; frequency, 60 cy; 115 v; ac; single phase. Made by the Sola Electric Company, Chicago, Illinois. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in conjunction with colorimeter for constant voltage.

Vacuum Pumping System. The pumps used in the evacuation of the various parts of the system are as follows:

Hyvac. Cenco, 10 liters per minute capacity, 350 rpm, equipped with a 1/4 hp, 115 v, 60 cy, ac, 1750 rpm motor. Obtained from Central Scientific Company, Chicago, Illinois. One used in conjunction with the operation of the McLeod gage, and one used in evacuating the distillate product tank after each fraction was removed from the still.

Megavac. Cenco, 31 liters per minute capacity, 325 rpm, equipped with a 1/4 hp, 115 v, 60 cy, ac, 1750 rpm motor. Obtained from Central Scientific Company, Chicago, Illinois. Two megavacs used in parallel as forepumps for diffusion pumps.

Diffusion. Metal, vertical, 500-milliliter oil capacity, 115 v, 60 cy, ac heater, water-cooled. Other specifications unknown. Obtained from war surplus. Manufactured by Consolidated Vacuum Corporation (formerly Distillation Products Industries), Rochester, N. Y. Two diffusion pumps used in series to obtain ultimate vacuum in system.

Voltage Stabilizer. Raytheon, type VR-6114, 250 w capacity, 90 to 130 v, 60 cy, ac. Obtained from the Walter Ashe Radio Company, St. Louis, Missouri. Used to stabilize current to variable speed rotor motor.

Method of Procedure

The methods of procedure followed in the performance of this study are explained under the headings of (1) preliminary design and construction of an all-metal still based on the Coli(15) design and recommendations; (2) modifications to the all-metal unit to include the motor drive within the vacuum system; (3) preliminary tests; (4) operational procedure; (5) operational instructions; and (6) analysis procedure.

Preliminary Design and Construction of an All-Metal Molecular Still Based on the Coli Design and Recommendations. After a study of the design and construction features of the centrifugal molecular still constructed and operated by Coli and of his recommendations for improvement in design was made, it was decided to construct the unit as a complete all-metal unit, with the exception of the bell jar, in an effort to minimize leaks. The basic design features of Coli's still were used throughout the design of the all-metal unit and a number of his recommendations, particularly those that could be applied to the all-metal unit, such as silver soldering of all tube to base plate connections, providing additional head in feed line to feed pump to improve flow conditions, increasing rotor heater capacity, and inserting valves at various points to isolate a particular portion of the system to aid in checking for leaks, were included in the new design. The manner in which these features and several others were included into the new design are discussed under the appropriate headings that follow. The frame(24) that served as the mount for the still, the bearing mount(24), the aluminum rotor(22), the rotor shaft and support(23), the gutter(20), the rotor heater shell(25), and the base plate(18) as designed by Coli were incorporated into the new design.

Replacement of Glass Flow System with Copper and Brass as Materials of Construction. In order to avoid glass-to-metal seals, the reconstruction of the reservoirs, flow lines, valves, and feed pump were of copper and/or brass construction.

Feed and Residue Reservoirs. Two copper tanks, 4 inches high, were constructed from 4-inch copper pipe. The top and the slightly concaved bottom of the tanks were made of 1/8-inch copper plate, silver-soldered into place. Holes were drilled into the reservoirs at the appropriate points for the necessary connections of flow and vacuum lines to accommodate 1/4-inch tubing adapters, as shown in Drawings 1 and 2, pages 91 and 92. The adapters were silver-soldered into place and the necessary tubing flow lines were then silver-soldered into the adapters. A 1/4-inch valve, V-3, was placed in the line between the residue tank, I, (top tank) and the feed tank, S, (bottom tank) so that they could be isolated

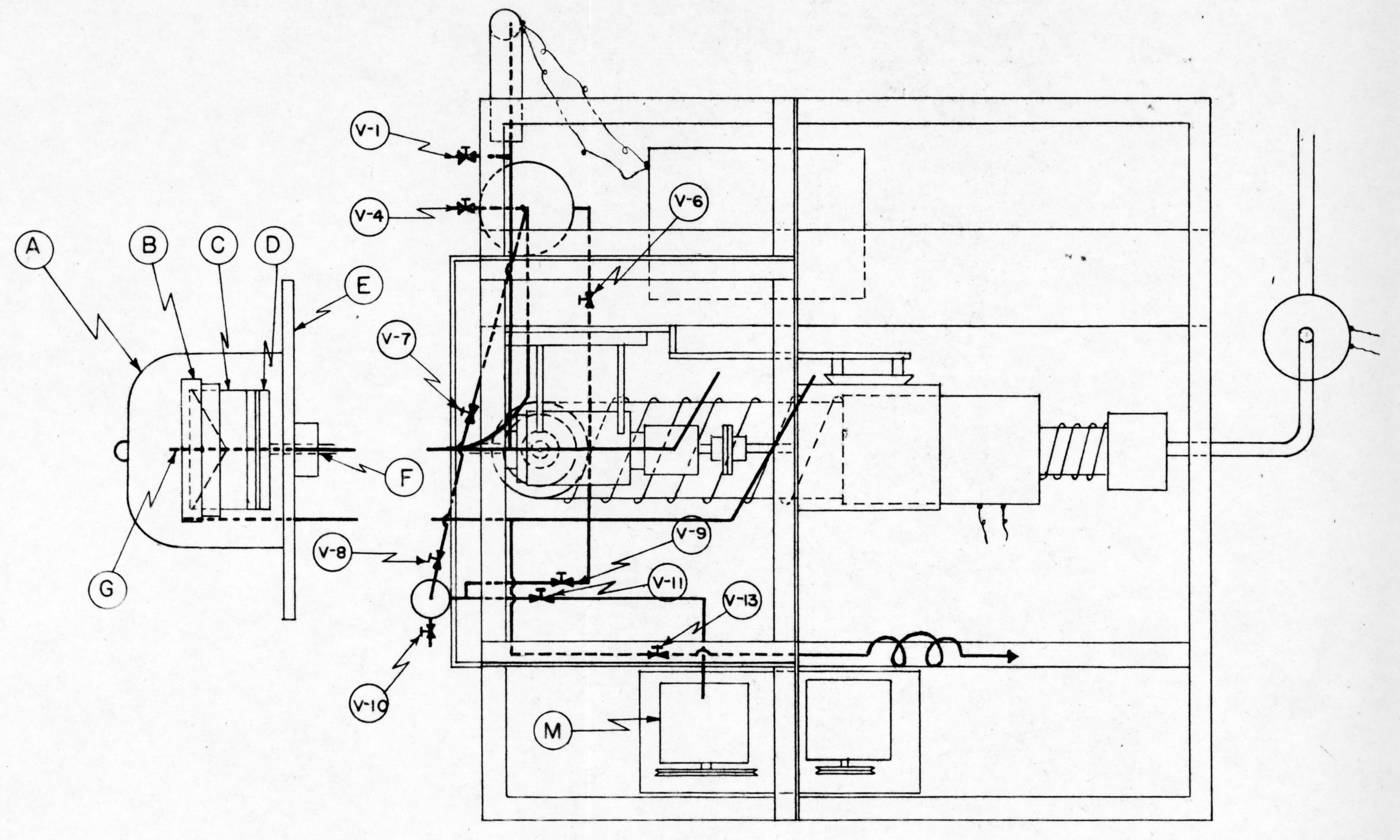
NOTES

① STILL HEAD ASSEMBLY DISPLACED IN PLAN VIEW FOR CLARITY.

② ALL PIPE LINES 1/4" COPPER TUBING.

③ ALL TUBING SHOWN IN HEAVY LINES FOR CLARITY.

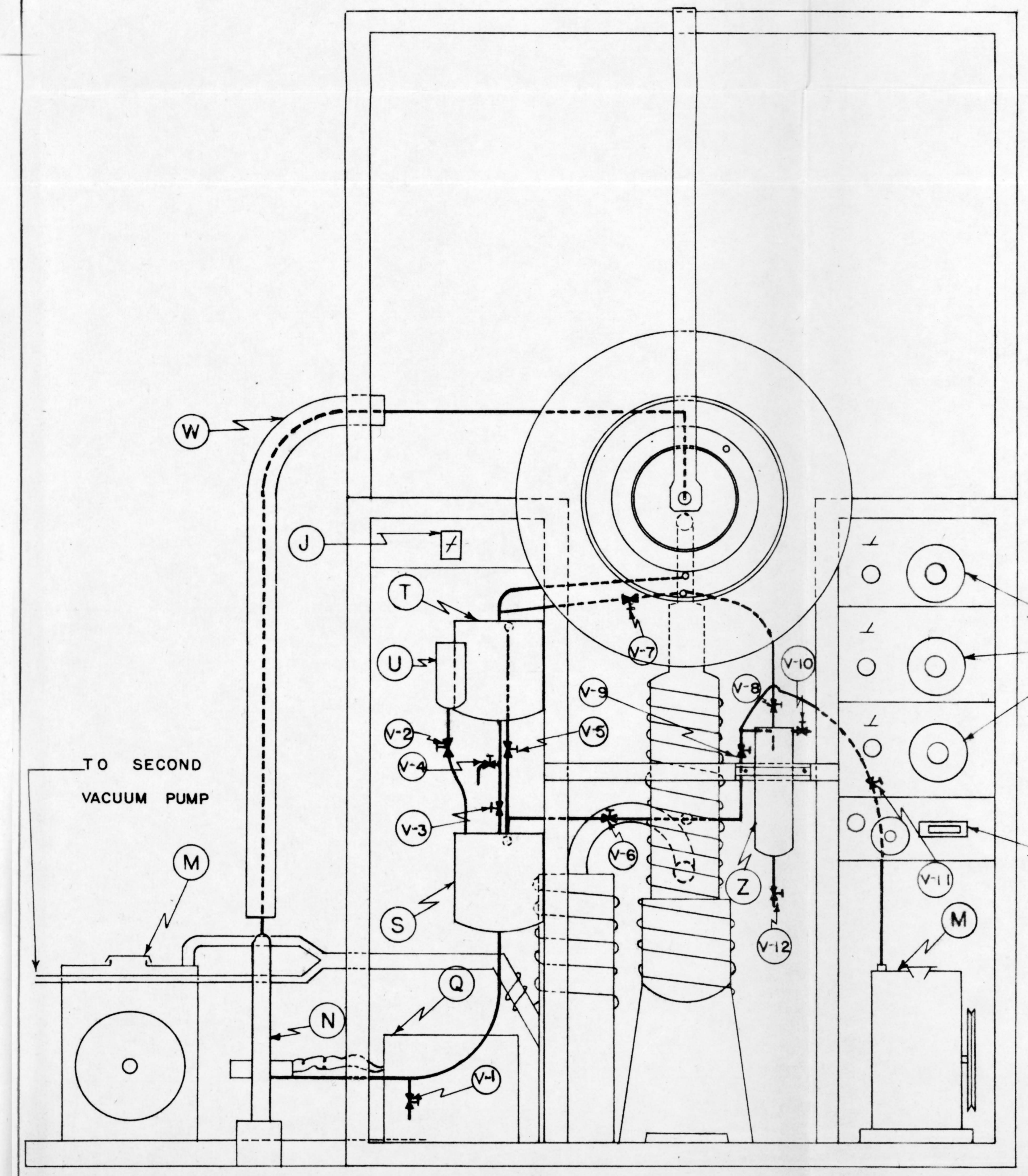
④ FRAME CONSTRUCTED FROM 1" X 1" X 1/8" STEEL ANGLE IRON.



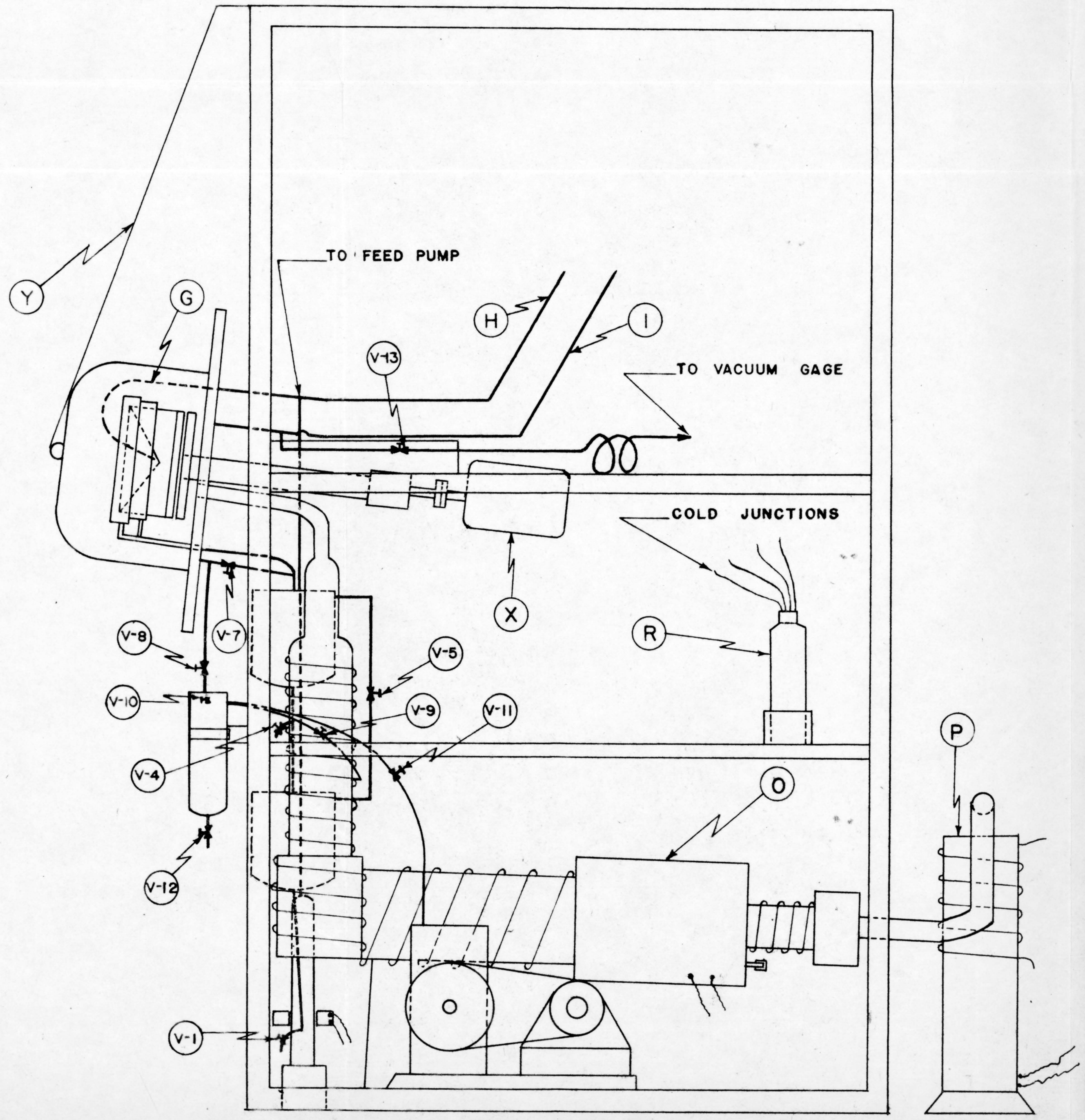
PLAN VIEW

KEY TO SYMBOLS

Ⓐ	BELL JAR
Ⓑ	DRAIN GUTTER
Ⓒ	ROTOR
Ⓓ	ROTOR HEATER
Ⓔ	BASE PLATE
Ⓕ	SHAFT
Ⓖ	FEED LINE
Ⓗ	FEED THERMOCOUPLE
Ⓘ	RESIDUE THERMOCOUPLE
Ⓙ	THERMOCOUPLE SELECTOR SWITCH
Ⓚ	POWERSTATS
Ⓛ	MAIN SWITCH
Ⓜ	VACUUM PUMP
Ⓝ	FEED PUMP
Ⓞ	PRIMARY DIFFUSION PUMP
Ⓟ	SECONDARY DIFFUSION PUMP
Ⓠ	D.C. POWER BOX
Ⓡ	THERMOS BOTTLE
Ⓢ	FEED TANK
Ⓣ	RECYCLE TANK
Ⓤ	LOADING TANK
Ⓦ	FEED PREHEATER
Ⓧ	ROTOR MOTOR
Ⓨ	BELL JAR STRAP
Ⓩ	COLLECTING TANK
Ⓥ	VALVES
(V-1)	FEED TANK DRAIN VALVE
(V-2)	LOADING TANK VALVE
(V-3)	RECYCLE RETURN VALVE
(V-4)	RECYCLE TANK DRAIN VALVE
(V-5)	PRESSURE EQUILIZING VALVE
(V-6)	VACUUM LINE VALVE
(V-7)	RECYCLE VALVE
(V-8)	COLLECTING VALVE
(V-9)	DIFFUSION PUMP VALVE
(V-10)	COLLECTING TANK VENT VALVE
(V-11)	VACUUM PUMP VALVE
(V-12)	COLLECTING TANK DRAIN VALVE
(V-13)	VACUUM GAGE VALVE



FRONT ELEVATION



RIGHT SIDE ELEVATION

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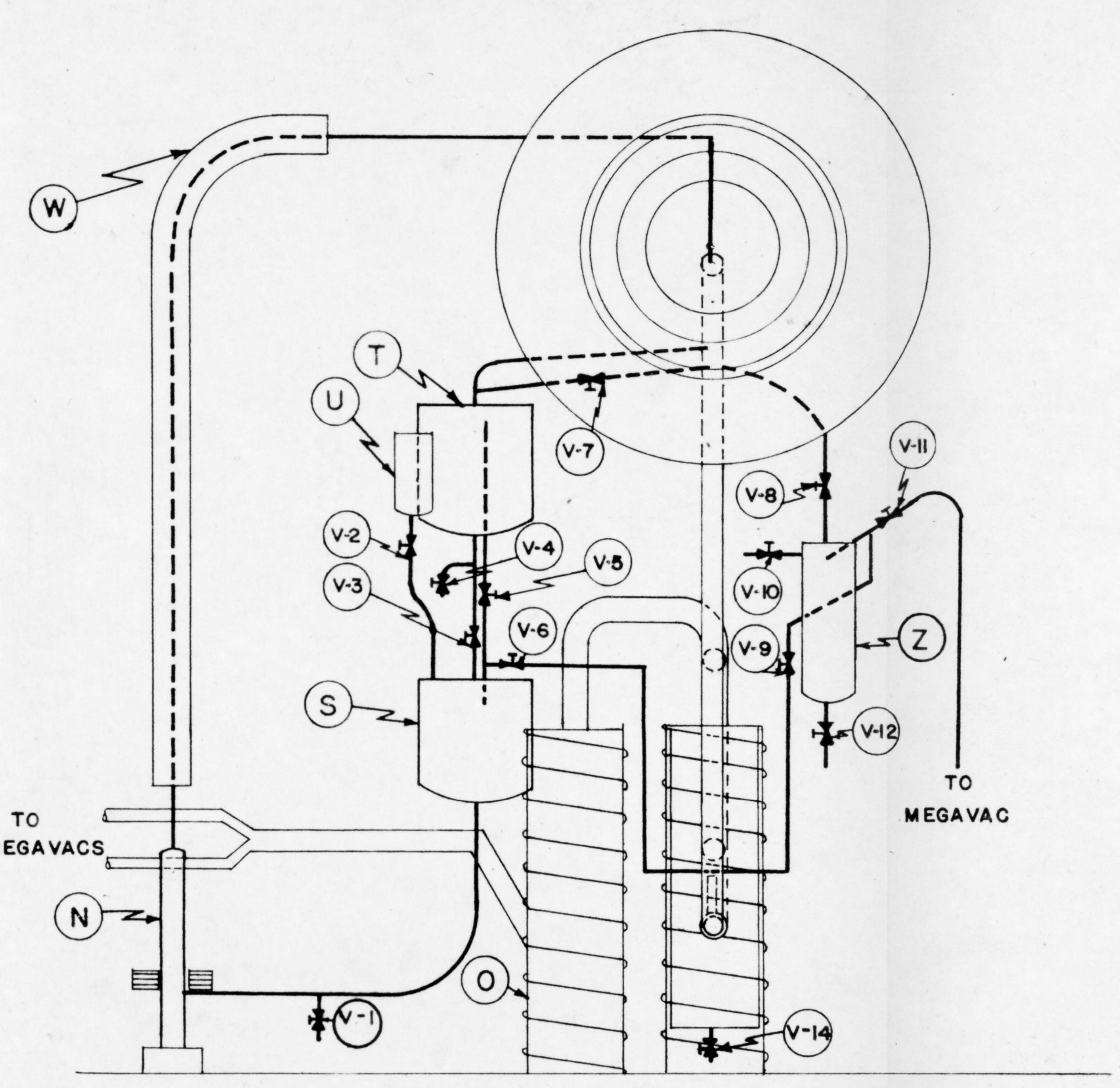
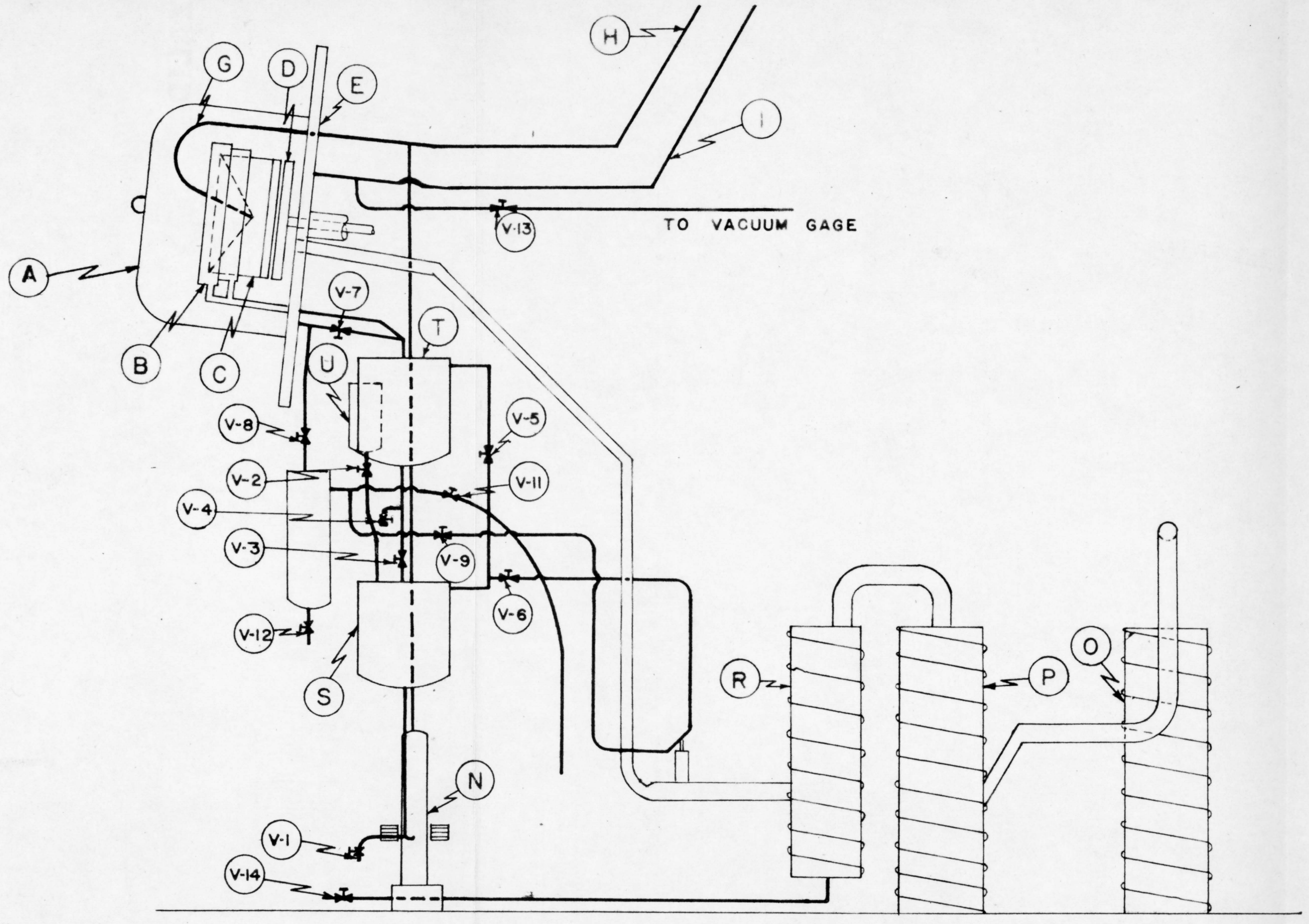
CENTRIFUGAL MOLECULAR STILL

SCALE: 3/16" = 1" DATE
DRAWN BY: JJS 1/13/53
CHECKED BY: JWB 1/13/53
APPROVED BY: F.C.V 1/14/53

CASE NO. 53
FILE NO. 799
DRAWING NO. 1



FRONT ELEVATION



RIGHT SIDE ELEVATION

KEY TO SYMBOLS

Ⓐ	BELL JAR
Ⓑ	DRAIN GUTTER
Ⓒ	ROTOR
Ⓓ	ROTOR HEATER
Ⓔ	BASE PLATE
Ⓖ	FEED LINE
Ⓗ	FEED THERMOCOUPLE
Ⓘ	RESIDUE THERMOCOUPLE
Ⓝ	FEED PUMP
Ⓞ	PRIMARY DIFFUSION PUMP
Ⓟ	SECONDARY DIFFUSION PUMP
Ⓡ	COLD TRAP
Ⓢ	FEED TANK
Ⓣ	RECYCLE TANK
Ⓤ	LOADING TANK
Ⓥ	VALVES
Ⓦ	PREHEATER
Ⓩ	COLLECTION TANK

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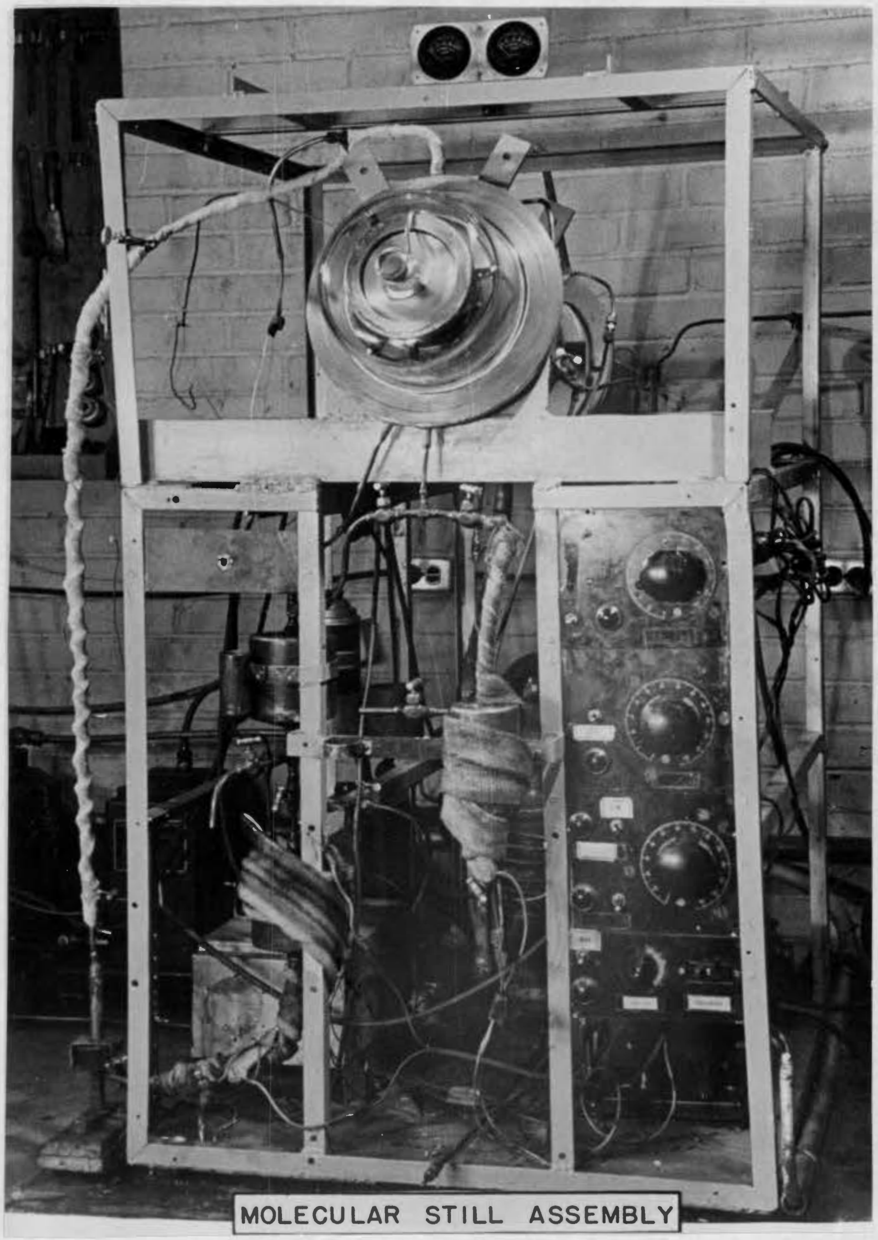
MODIFIED PIPING DIAGRAM
FOR
CENTRIFUGAL MOLECULAR STILL

SCALE: 3/16" = 1" DATE
DRAWN BY: JJS 1/13/53
CHECKED BY: JWB 1/13/53
APPROVED BY: F.C.V. 1/14/53

CASE NO. 53
FILE NO. 799
DRAWING NO. 2



Photograph 1. Molecular Still Assembly

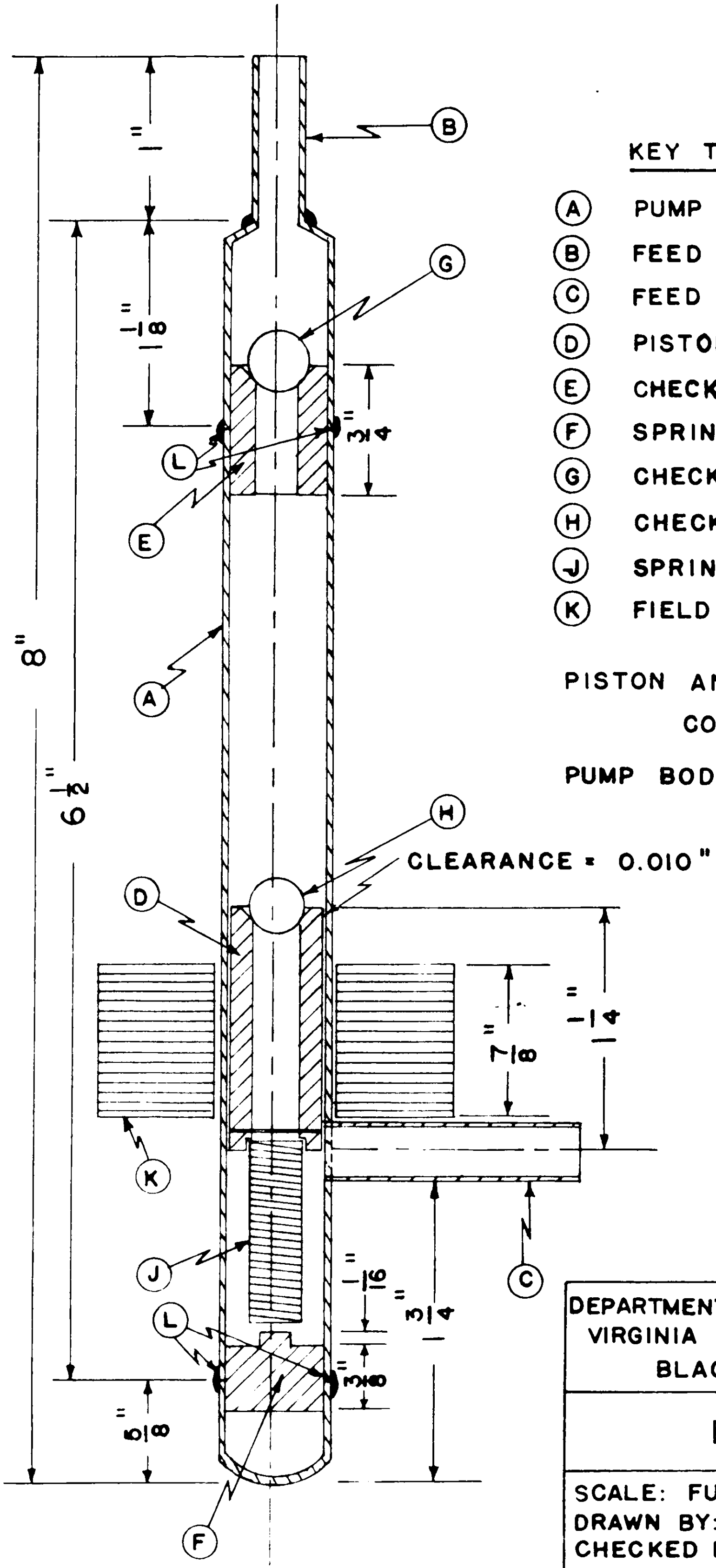
when the vacuum system was being checked for leaks and to make use of the tanks in calibrating the feed pump. A feed loading tank, U, was constructed from a 3-inch length of 1-1/2 inch copper tubing, open at one end and having a slightly concave bottom for drainage purposes. This tank was connected at the feed tank, S, by 1/4-inch copper tubing and valve V-2. The capacity of the feed and residue tanks was 825 milliliters each and that of the loading tank was 100 milliliters.

Distillate Reservoir. In a preliminary reconstruction of the still assembly and accessories, two 100-milliliter capacity collection tanks were installed for the purpose of distillate collection. These were connected to a common drain from the base plate of the still and were properly valved to collect alternate fractions of product. Preliminary operational tests indicated that one collection tank was sufficient. It was found that one tank would serve to simplify the operational procedure, to lessen the number of connections and valves between the tanks and thereby decrease the possibilities of leaks, and to decrease the drainage error encountered because of the necessary manifold line connecting the two tanks. Accordingly, a collection tank, Z, was constructed from a 5-inch length of 2-inch copper pipe to which was silver-soldered a flat top and a slightly concaved bottom made from 1/8-inch copper plate. Holes were drilled at appropriate points for the 1/4-inch product inlet, drain, vacuum, and vent lines as shown in Drawings 1 and 2, pages 91 and 92. The capacity of the tank was 250 milliliters.

Flow Lines. In reconstructing the still, 3/16-inch copper tubing, Swagelok fittings, and compression-type connection globe valves were used in the assembly of the necessary flow and vacuum lines. The size of the tubing was too small to permit sufficient flow and drainage with the head available and was replaced with 1/4-inch copper tubing and the correspondingly larger size valves. This change in design necessitated the use of compression-type fittings throughout the new construction. The compression-type fittings were tested and found to be unsatisfactory for maintaining vacuum-tight seals and they were replaced by silver-soldered joints. The valves in the system were also silver-soldered into the tubing flow lines. The flow lines, the valves, and the number of connections in the final assembly were reduced to a minimum in an attempt to reduce potential leaks and to facilitate more simple operation of the apparatus. These flow lines are best shown as the heavy lines in the modified piping diagram, Drawing 2, page 92.

Feed Pump. A small, glass, magnetically operated pump used by Coli(15) was replaced in the preliminary design of the all-metal system by a single-acting, Hills-McCanna proportioning pump. Unsuccessful attempts were made to pump the distilland from the feed tank, S, to the rotor, C, Drawing 1, page 91, while the system was at an absolute pressure of 10 microns of mercury. The reciprocating piston in the body of the pump was not sufficiently sealed to allow the pump to operate against a suction head of greater than 10 feet of water, 225 millimeters of mercury. The modifications to the body of the pump and piston seal necessary to permit the pump's operation at 1 to 10 microns absolute pressure would have required more constructional changes and time than the construction of an all-metal, magnetically-operated pump similar in design to the glass pump used by Coli. A detailed explanation of the operation of the pump is given by Coli(26).

The all-metal pump that was constructed consisted of a copper body, steel piston, steel ball-check valve seats, and brass balls as shown in Drawing 3, page 97.



KEY TO SYMBOLS

- Ⓐ PUMP BODY TUBING (0.5500" I.D.)
- Ⓑ FEED OUTLET TUBING
- Ⓒ FEED INLET TUBING
- Ⓓ PISTON WITH 1/4" BORE
- Ⓔ CHECK VALVE SEAT } PRESS FIT
- Ⓕ SPRING STOP } PRESS FIT
- Ⓖ CHECK BALL } 5/16" DIAMETER
- Ⓗ CHECK BALL } 5/16" DIAMETER
- Ⓙ SPRING
- Ⓚ FIELD COIL

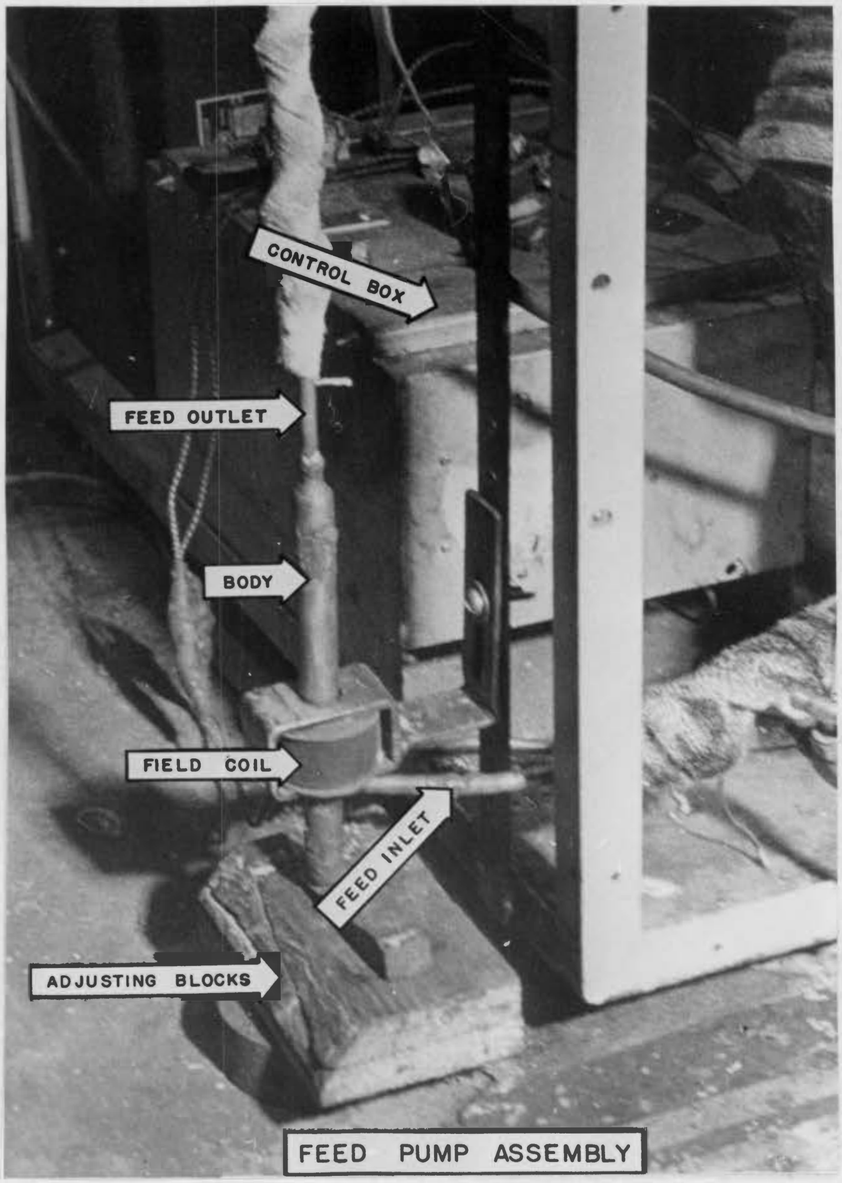
PISTON AND CHECK VALVE SEATS COUNTERSUNK 82°

PUMP BODY SOLDERED AT Ⓛ

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

FEED PUMP

SCALE: FULL SIZE	DATE	
DRAWN BY:	1-13-53	CASE NO. 53
CHECKED BY:	1/13/53	FILE NO. 799
APPROVED BY:	[illegible]	DRWG NO. 3

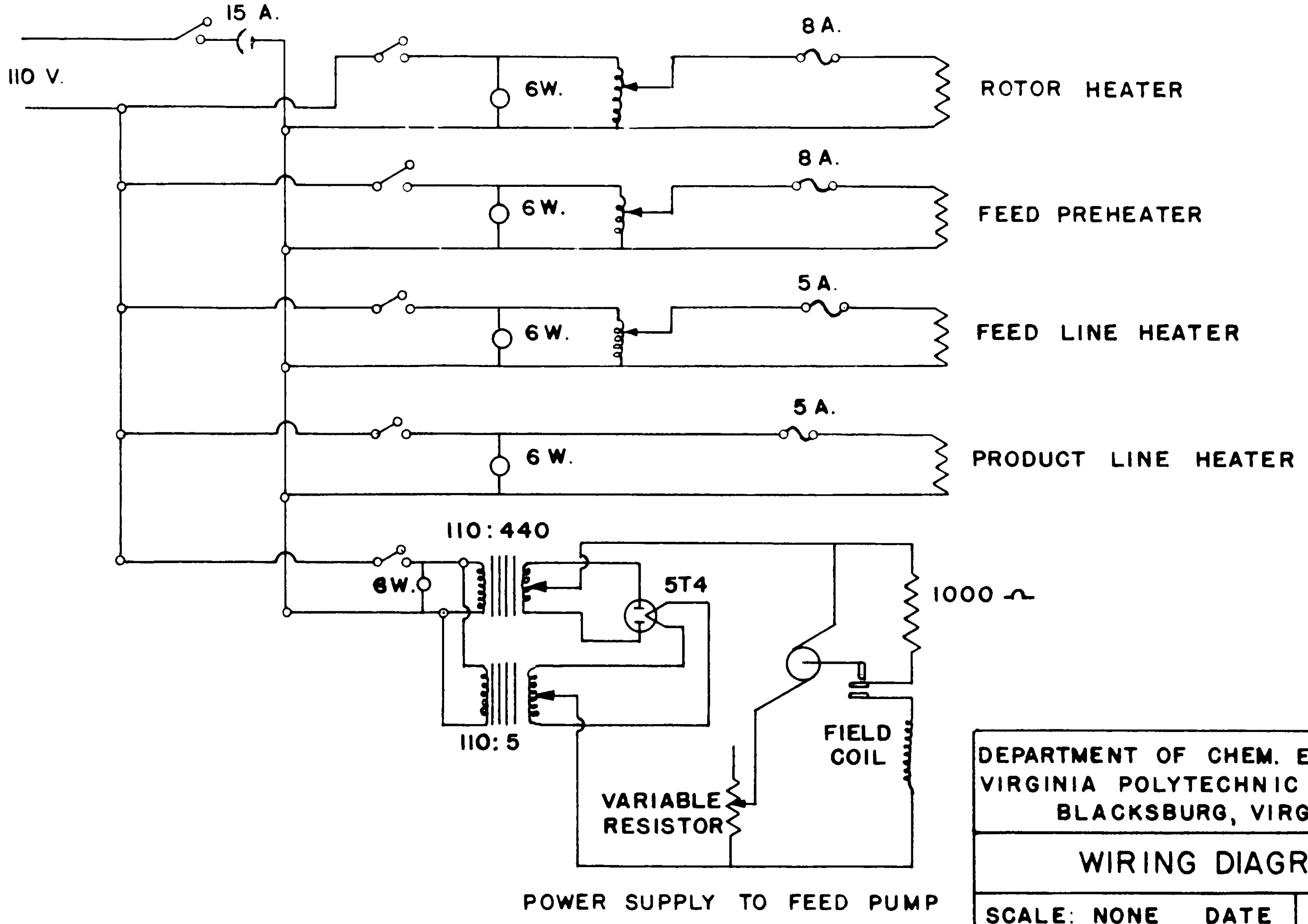


Photograph 2. Feed Pump Assembly

Complete details and dimensions of the pump are shown in the drawing. The piston of the pump was actuated by a field coil connected to an electrical "make-and-break" system, the wiring diagram of which is shown in Drawing 4, page 100.

Still Head Assembly. The still head was assembled as shown in Drawing 5, page 101. Modifications of the still head assembly from that used by Coli(17) included the use of all-welded connections for the vacuum lines, flow lines and rotor housing, the use of spark plugs tapped into the base plate for heater lead attachment, gutter modifications, the use of a silicone gasket for vacuum seal of the bell jar to the base plate, and the use of a copper feed nozzle.

Flow Lines and Rotor Housing Connections to Base Plate. The base plate was drilled and tapped to accommodate the rotor housing which was threaded with 1 1/4-12NC-2 threads. A 1-inch copper pipe-to-tubing adapter was threaded into the base plate, immediately below the rotor housing inlet for the diffusion pump connection. The same flow line inlets and outlets as used by Coli(17) were drilled, tapped, and fitted with 1/4-inch adapters. These adapters as well as the rotor housing and diffusion pump connection were silver-soldered into the plate to eliminate potential leaks.



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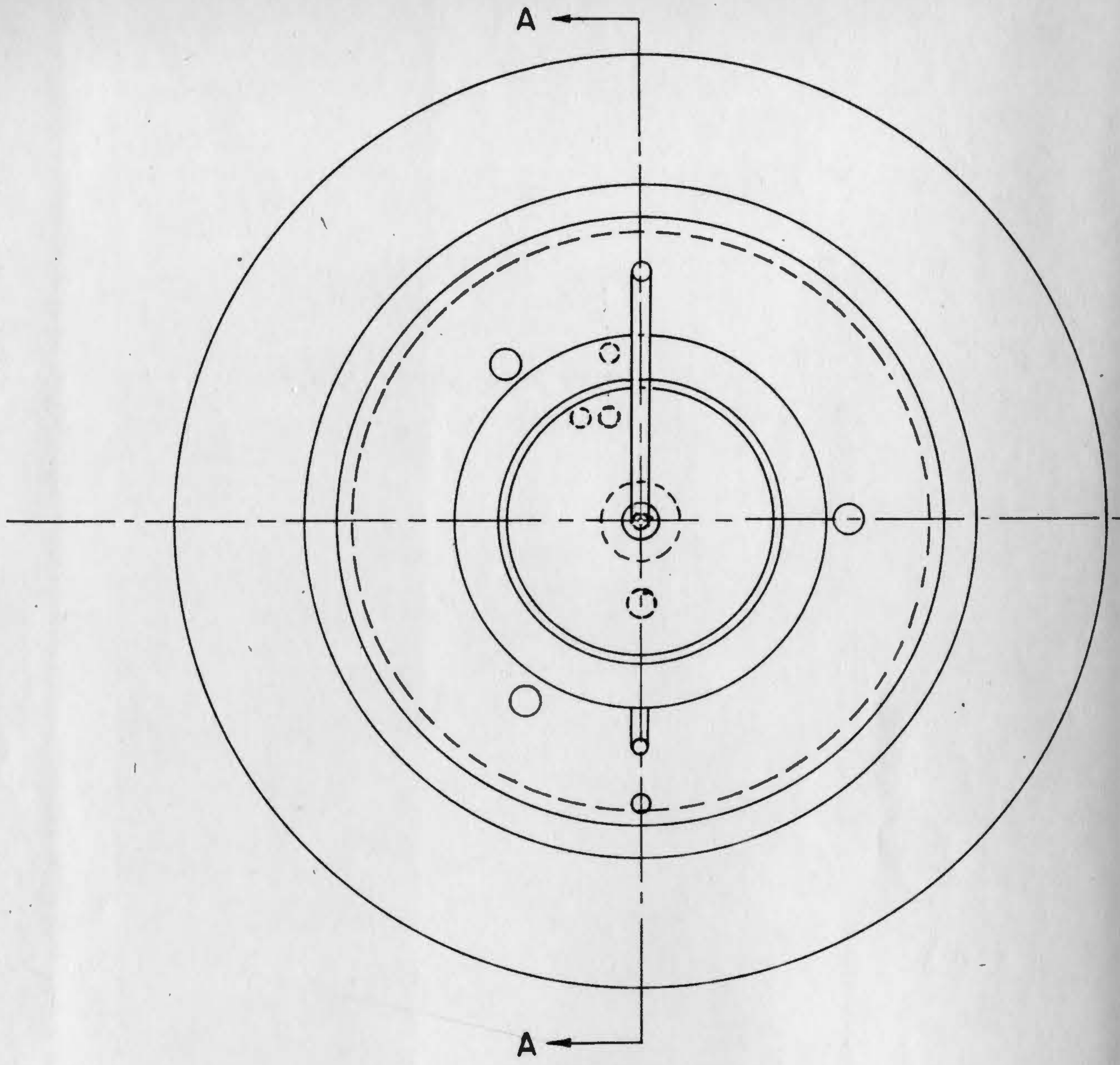
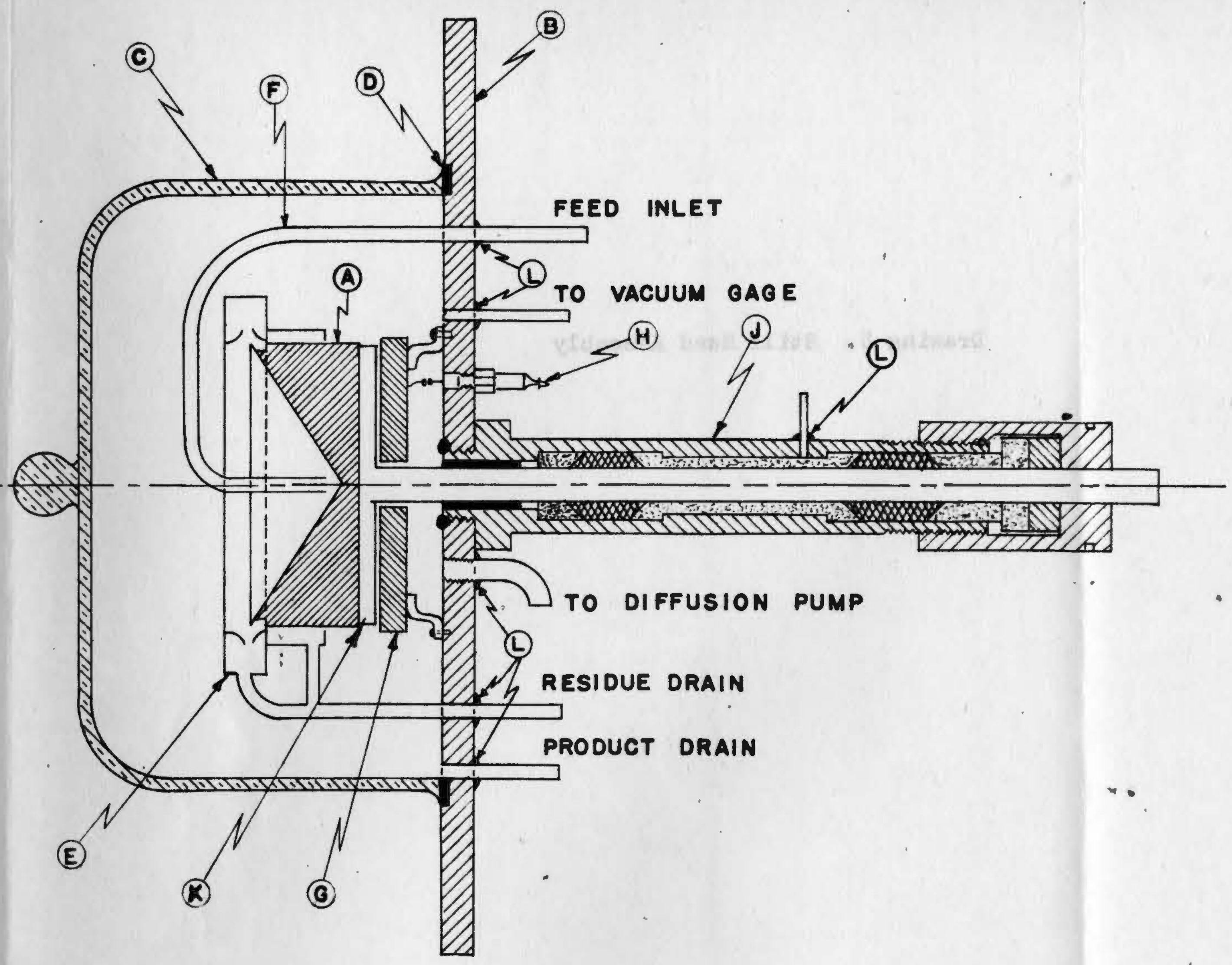
WIRING DIAGRAM

SCALE: NONE	DATE	
DRAWN BY: JLD	1-13-53	CASE NO. 53
CHECKED BY: JWB	1/13/53	FILE NO. 799
APPROVED BY: F.C.V.	1/14/53	DRWG NO. 4



FRONT VIEW



SECTION A-A

LEGEND

Ⓐ	ROTOR	Ⓕ	FEED NOZZLE
Ⓑ	BASE PLATE	Ⓖ	ROTOR HEATER
Ⓒ	PYREX GLASS BELL JAR	Ⓗ	SPARK PLUG
Ⓓ	SILICONE GASKET	Ⓙ	ROTOR SHAFT (SEE DRAWING , PAGE)
Ⓔ	GUTTER	Ⓚ	ROTOR SUPPORT

Ⓛ SILVER SOLDERED

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STILL HEAD ASSEMBLY

SCALE: 3/8" = 1" DATE
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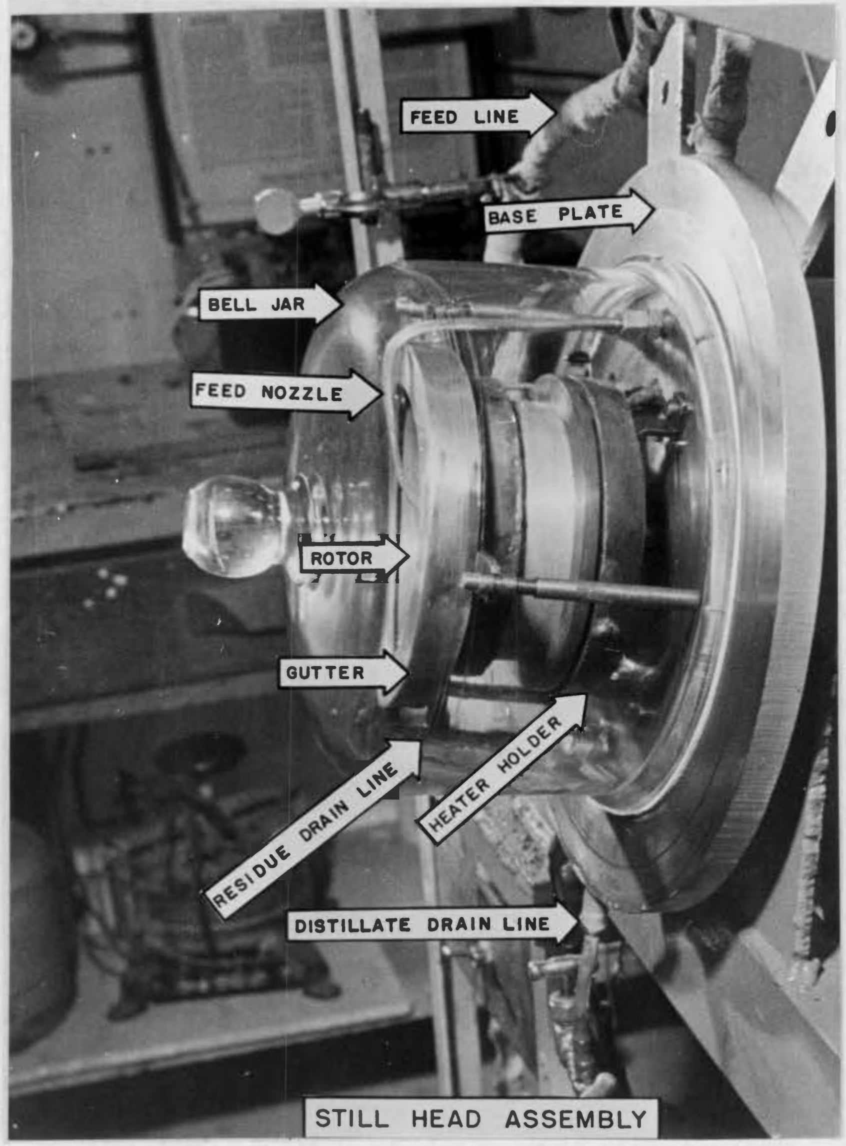
CHECKED BY: 1/13/53
APPROVED BY: T.C.V. 1/14/53

CASE NO. 53
FILE NO. 799
DRWG NO. 55



Photograph 3. Still Head Assembly

Heater Lead Connections. Coli experienced considerable difficulty in maintaining vacuum seals around the heater leads through the base plate. In order to eliminate this source of leaks, the base plate was drilled and tapped to accommodate two No 45 AC spark plugs. To insure a vacuum-tight seal, the holes for the spark plugs at the back side of the plate were counterbored to a depth of 1/8-inch with a flat-end boring tool making a flat shoulder for the plugs to press against. The diameter of the counterbored hole was 1/16-inch greater than the base of the spark plugs. In assembling the spark plugs in the base plate, a lead washer 1/2-inch inside diameter and 3/4-inch outside diameter and 1/8-inch thick was slipped into the counterbore. The spark plugs were then inserted and tightened into place forcing the lead gasket against the flat shoulder and into the clearance between the plugs and the plate, thus insuring a vacuum-tight seal.

Prior to assembly, the side contacts of the spark plugs were removed and a 1/2-inch length of a 10/24-inch bolt was silver-soldered to the central terminal of each spark plug for attachment of the heater leads.

Gutter Modifications. The modified gutter, E, is shown in the still head assembly diagram, Drawing 5, page 101. A 3/4-inch copper sleeve with a 1/4-inch lip was silver-soldered to the back of the gutter used by Coli(20). A 5/16-inch copper tubing outlet at the bottom of the sleeve aligned and connected with the gutter drain line served for drainage. This sleeve extension served to catch any drippings or overflow from the gutter proper. A compression-type ferrule fitting was secured to the end of the gutter drain line for attachment to the adapter in the base plate.

Bell Jar Seal. After the modifications to the base plate were made, it was necessary to reface the front of the base plate for alignment with the new shaft and rotor bearing housing. Naturally, in refacing the plate, the ground glass-to-metal surface used by Coli for vacuum-tight connection of the bell jar to the base plate was removed. Accordingly, the bell jar was reground to the base plate using a fine polishing grade of valve grinding compound. Attempts to use the ground glass-to-metal connection and vacuum grease for sealing the bell jar to the base plate were unsuccessful. When the system was placed under high vacuum, the bell jar was pulled so tightly against the grease-lubricated ground joint that the glass actually bonded to the metal. When the vacuum was released, the glass would chip out of the bell jar bearing surface in very thin slivers and adhere firmly to the base plate. The bell jar surface soon showed gouges from the inside to the outside of the ground surface making it worthless for vacuum work. Thus, it was decided to use a 1/8-inch thick silicone gasket to effect the seal. A groove, 7-7/8 inches inside diameter by 9 inches outside diameter by 1/8-inch deep was machined into the base plate to accommodate the gasket and to help to center and hold it in place beneath the bearing surface of the bell jar. The gasket is shown in place between the bell jar and the base plate as item D, Drawing 5, page 101.

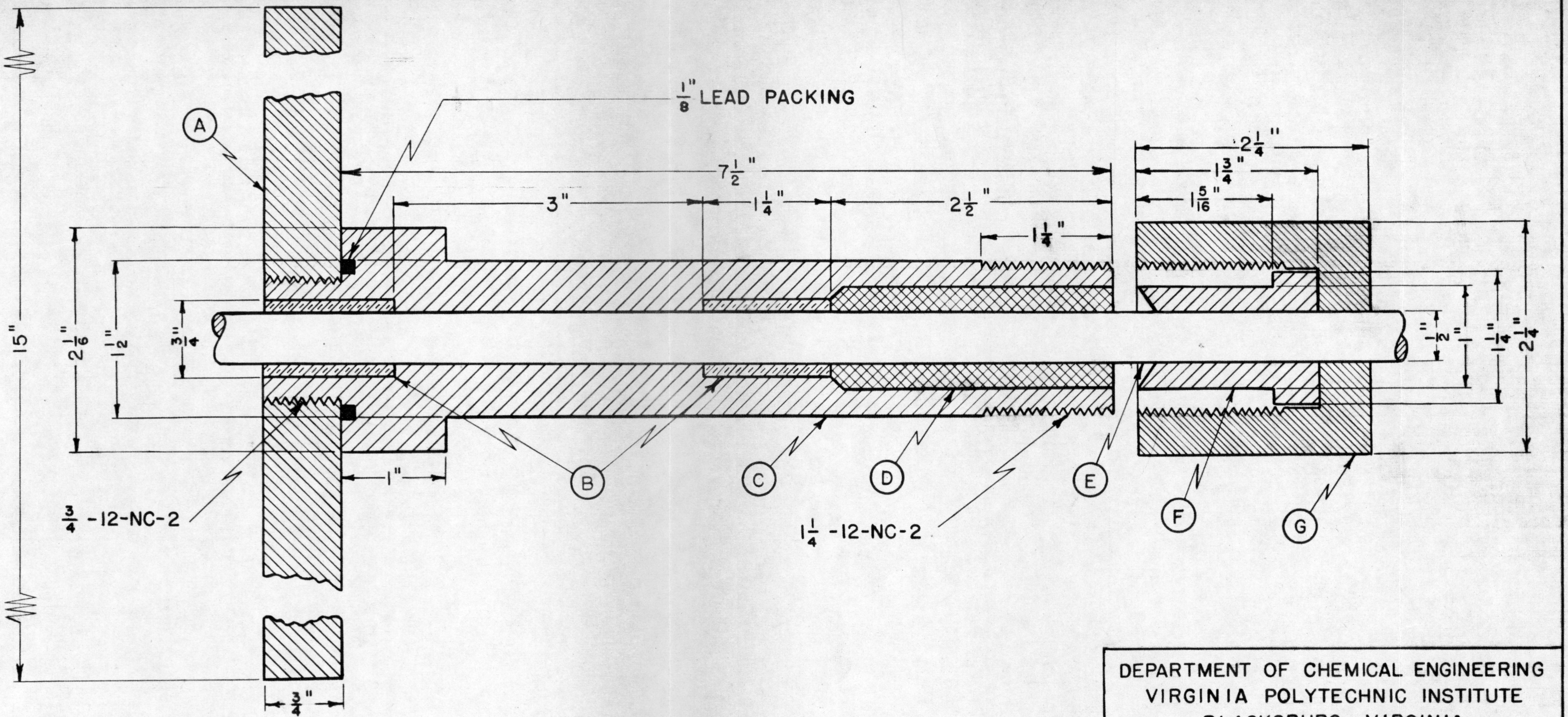
Feed Nozzle. In the tests made by Coli(28), a glass feed nozzle made from a 1/4-inch length of 0.25 millimeter bore capillary on the end of the glass feed tube gave best results. It was desired in the redesign to make a metal feed tube and nozzle for ease of connection to an adapter in the base plate. Accordingly, three feed tubes were made from 3/16-inch copper tubing to which 1/4-inch lengths of 1/16-inch copper tubing were silver-soldered. One nozzle was drilled with a No 56 drill

(0.0465-inch), one with a No 58 drill (0.0420-inch), and the third with a No 60 drill (0.0400-inch). The three feed tubes thus constructed were tested in the system for flow characteristics. The nozzle with the smallest opening gave droplet flow while the one with the largest opening gave flow in surges for an average flow rate of 15 milliliters per minute. It was reasoned from the fact that the flow changed from droplets to surges that the flow could be made smooth by redesign of the feed tube with an enlarged nozzle. In order to eliminate a considerable amount of resistance caused by the presence of the 1/4-inch length of small bore tubing, serving as the nozzle proper, one end of a new length of 3/16-inch tubing was peened nearly closed, covered with a thin film of silver solder, and then drilled with the No 60 drill. The flow characteristics of this nozzle were tested and also found to be unsatisfactory in that surge flow still persisted. Successively larger drills (1/32, 3/64, 1/16, and 5/64-inch) up to 3/32-inch were used in making the nozzles larger, flow tests being made after each enlargement. It was found that the 3/32-inch nozzle gave a nearly uniform pattern despite the reciprocating action of the feed pump. The flow rate of light mineral oil through this nozzle could be varied from 40 to 125 milliliters per minute.

Heater Shell and Rotor Plate. The rotor heater shell, G, Drawing 5, page 101, designed and used by Coli(25), was used in this investigation. However, a new type of heater element, to be described later, was used for heating the rotor. The rotor plate, K, and the shaft arrangement(23) were also used as originally designed.

Rotor Housing. The rotor housing proper was completely redesigned as shown in Drawing 6, page 108. Instead of having the packing in the tightening nut(21), it was placed in the rotor housing and a self-centering floating head in the tightening nut was used to force the packing tightly around the shaft as the tightening nut, G, was tightened into the plate. This design eliminated the eccentric effect of the threaded connection of the housing and tightening nut.

Preliminary Design. In the preliminary design, the body of the rotor housing, C, was made from steel rod stock 8-1/4 inches long by 2-1/4 inches diameter. The end to be secured to the base plate was cut back a distance of 3/4-inch to 1 inch in diameter and threaded



LEGEND

Ⓐ	PLATE	Ⓔ	SHAFT (CLEARANCE = 0.0002")
Ⓑ	BEARING	Ⓕ	SELF-CENTERING PACKING NUT HEAD
Ⓒ	HOUSING	Ⓖ	TIGHTENING NUT
Ⓓ	PACKING		

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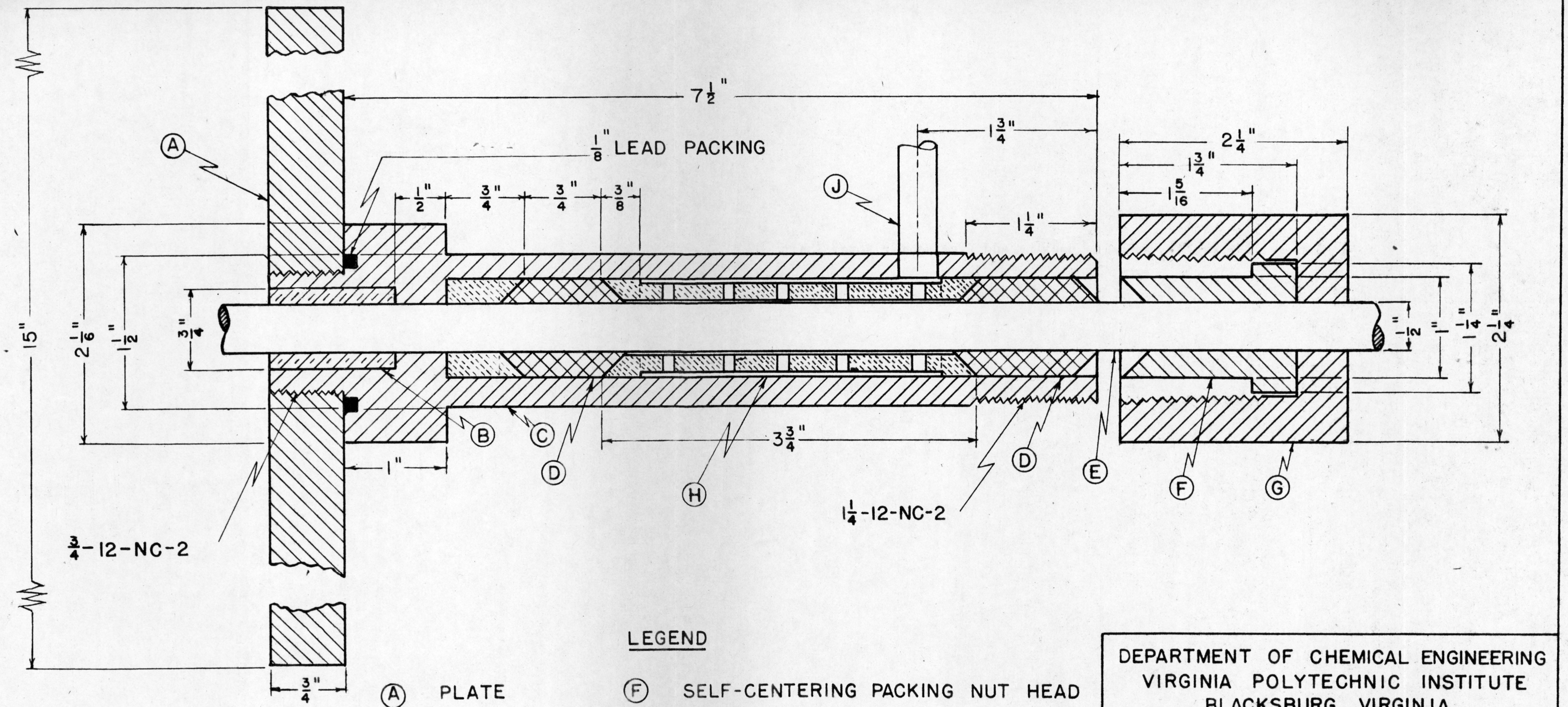
DETAILS OF BEARING AND PACKING
FOR ROTOR SHAFT

SCALE: FULL SIZE
DRAWN BY: GJD DATE: 7/9/52
CHECKED BY: JWB DATE: 1/13/53
APPVD BY: FCV. DATE: 1/14/53

CASE: 53
FILE: 799
DRWG NO: 6

with No 12-NC-2 threads. A section, 1 inch long, adjacent to the threaded section was made 2-1/16 inches in diameter to serve as a shoulder in aligning the assembly in the housing mount(24). The remainder of the length of the housing was made 1-1/2 inches in diameter to fit the housing mount and the last 1-1/4 inches of length (on the end away from the base plate) was threaded with No 12-NC-2 threads to accommodate the tightening nut. A hole was then machined through the center of the stock to accommodate the 1/2-inch shaft, *E*, with a clearance allowed of approximately 0.0010 inch. The base plate end of the housing was then machined to accommodate a pressed, flush fit of a 3/4-inch outside diameter by 1-1/4 inch long oilyte bearing, *B*. The opposite end of the housing was machined to accommodate a second oilyte bearing 3 inches from the first. From the outer edge of the second bearing, the housing was enlarged to 1 inch to accommodate the packing, *D*. The tightening nut, *G*, was made 2-1/4 inches long by 2-1/4 inches outside diameter and machined to accommodate the shaft, *E*, a self-centering floating head, *F*, and housing, *C*. The floating head, *F*, was made of bronze and machined to fit into the body of the housing to force the packing around the shaft when the nut, G, was tightened. The internal diameter of the floating head was machined to fit the shaft with a clearance of 0.0002 inch, forming an end-bearing surface for the shaft.

Modification of Preliminary Design. Tests of the system indicated that when the packing became hot and somewhat dry, vacuum leaks occurred around the shaft. Tightening of the packing around the shaft only caused stalling of the motor with no apparent reduction of the leaks. It was necessary, therefore, to modify the design of the housing to keep the shaft lubricated at all times during operation. The redesign, to include a lantern ring, H, is shown in Drawing 7, page 111. The back oilyte bearing was removed and the internal diameter of the housing was increased to 1 inch from the position occupied by the back oilyte bearing to within 3/8-inch of the front bearing. A 1-inch outside diameter by 1/2-inch inside diameter bronze collar 3/4-inch long with one end tapered 45 degrees toward the position of the shaft, was forced into position against the shoulder supporting the front oilyte bearing. A 3-3/4 inch bronze lantern ring, H, 1 inch outside diameter



LEGEND

Ⓐ PLATE

Ⓑ BEARING

Ⓒ HOUSING

Ⓓ PACKING

Ⓔ SHAFT (CLEARANCE = 0.0002")

Ⓕ SELF-CENTERING PACKING NUT HEAD

Ⓖ TIGHTENING NUT

Ⓗ LANTERN RING

Ⓙ GREASE INLET

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MODIFIED BEARING AND PACKING FOR ROTOR SHAFT

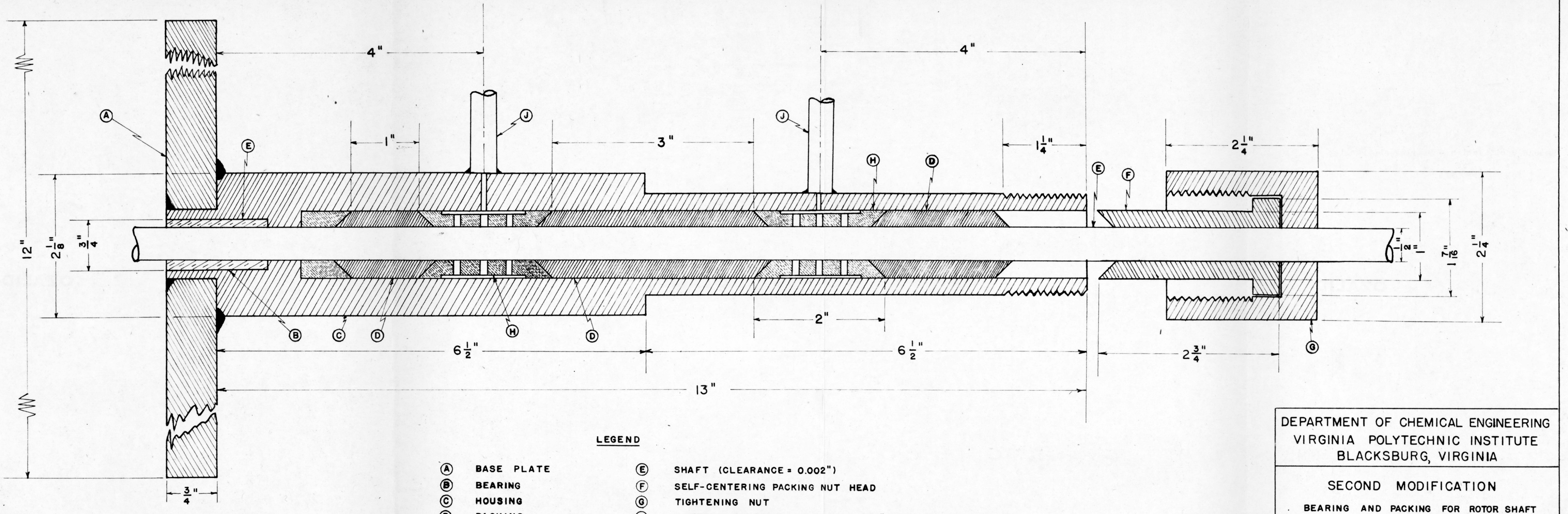
SCALE: FULL SIZE
DATE
DRAWN BY: GJD 1-13-53
CHECKED BY: JWB 1/13/53
APPROVED BY: T.C.V. 1/14/53

CASE: 53
FILE: 799
DRWG NO: 7

with a 3/8-inch long shoulder on each end and the inner portion between the shoulders 7/8-inch outside diameter to allow the lubricant to flow along the length of the ring, was construted. Four rows of five 1/8-inch diameter holes were drilled along the length of the small diameter of the lantern ring, 90 degrees apart to direct lubricant flow to the shaft. On the inside surface of the ring, beneath each hole, a circular groove, 1/8 inch wide and 1/16 inch deep was cut to insure lubricant shaft contact and a vacuum-tight seal while the shaft was rotating. Both ends of the ring were tapered 45 degrees to direct the packing against the shaft. A lubricant connection, a 3-inch length of 1/4-inch pipe, was brazed into the housing body directly over the lantern ring so as to be facing upward in the final arrangement of the base plate-rotor assembly.

A grease cup was secured to the pipe and the lubricant was supplied, as needed, to the shaft by tightening the cap of the grease cup. The ring was so designed as to obtain the majority of the seal from the shaft-lubricant contact with about 1-1/2 inches of shaft-packing contact at both ends of the ring serving to keep the lubricant in place.

Second Modification of Preliminary Design of Rotor Housing. The overall length of the original housing was 8-1/4 inches, however, it was learned(55) that in commercial units of similar size and construction the housing is 13 to 15 inches long. Therefore, the modified housing was made 13 inches long and designed so that the added length would allow the base plate to extend out from the unit proper making the connections at the back of the base plate more accessible for inspection and repair. Two lubricant connections, 1/4-inch pipe, were bronzed into the housing body, four inches from each end of the housing for use in conjunction with two lantern rings, each two inches long. A new rotor plate was made and a hard chrome-plated steel shaft, 15 inches long was secured to it. All of the necessary connections for feed inlet, residue and distillate outlets, vacuum outlet, and thermocouple inlet were assembled to the base plate in the same positions as before so that they could be secured to the accessory equipment with a minimum of change. This second modification of the rotor housing is shown in Drawing 8, page 114.



LEGEND

Ⓐ	BASE PLATE	Ⓔ	SHAFT (CLEARANCE = 0.002")
Ⓑ	BEARING	Ⓕ	SELF-CENTERING PACKING NUT HEAD
Ⓒ	HOUSING	Ⓖ	TIGHTENING NUT
Ⓓ	PACKING	Ⓗ	LANTERN RINGS (CLEARANCE = 0.002", GREASE RECESS = 0.0315")

Ⓙ GREASE INLETS

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SECOND MODIFICATION

BEARING AND PACKING FOR ROTOR SHAFT

SCALE: FULL SIZE	DATE	
DRAWN BY: FWB	4-6-53	CASE: 53
CHECKED BY: GYD	4-6-53	FILE: 799
APPROVED BY: F.C.V.	4-7-53	DRWG NO: 8

Assembly of Still Head and Rotor Housing. In the preliminary assembly of the rotor housing to the base plate, a 1/8 by 1/8-inch lead gasket, placed in an undercut in the rotor housing, Drawing 6, page 103, was used for sealing the rotor housing to the base plate. This joint proved to be a major source of leaks. As a result, the rotor housing was silver-soldered to the base plate at the bell-jar side of the plate as indicated. Precautions were taken to have the lubricant connection pointing up when the vacuum outlet was directly below the rotor housing before securing the housing to the base plate. A longitudinal section was machined from the bearing mount to accommodate the lubricant connection. When the base plate-rotor housing assembly was inserted into the bearing mount, proper alignment of all base plate connections was assured when the lubricant connection was slipped through the section in the bearing mount provided for it. The housing was secured into position in the mount by a set screw.

The *spark plugs*, used for heater lead connections, were inserted and secured into place in the base plate as described on page 103. The *rotor heater shell* was fastened to the base plate by three 1/4 by 1/4-inch screws. The chromalox ring-heater element was centered into position in the heater shell by three 1/4 by 3/4-inch screws extending through the sides of the heater shell by being spaced 120 degrees apart. Leads from the heater to each of the spark plug connections were secured into position.

The shaft, to which the rotor plate had been welded, was then passed through the opening in the center of the ring-heater element and heater shell into the bearing and rotor housing. The rotor was attached to the rotor plate by a 1/4 by 1/2-inch bolt through the center of the cone of the rotor. The residue thermocouple was inserted through a small hole in the back of the gutter to a position within the gutter for contact with the residue leaving the rotor. The gutter was then secured into proper alignment with respect to the rotor by connecting the drain line lead line to the adapter in the plate, which in turn, is connected to the line to the residue tank. The gutter is further supported by three brass rods, 1/2-inch diameter by 4-1/2 inches long which had been threaded into blind holes tapped into the base plate. The feed nozzle was then centered with respect to the rotor, 5/32-inch away from the apex and secured into position in the base plate adapter connected to the feed line. The silicone gasket was placed in the groove in the face of the base plate provided for it and the bell jar was placed into position on the gasket and temporarily held in position by strap, Y, Drawing 1, page 91.

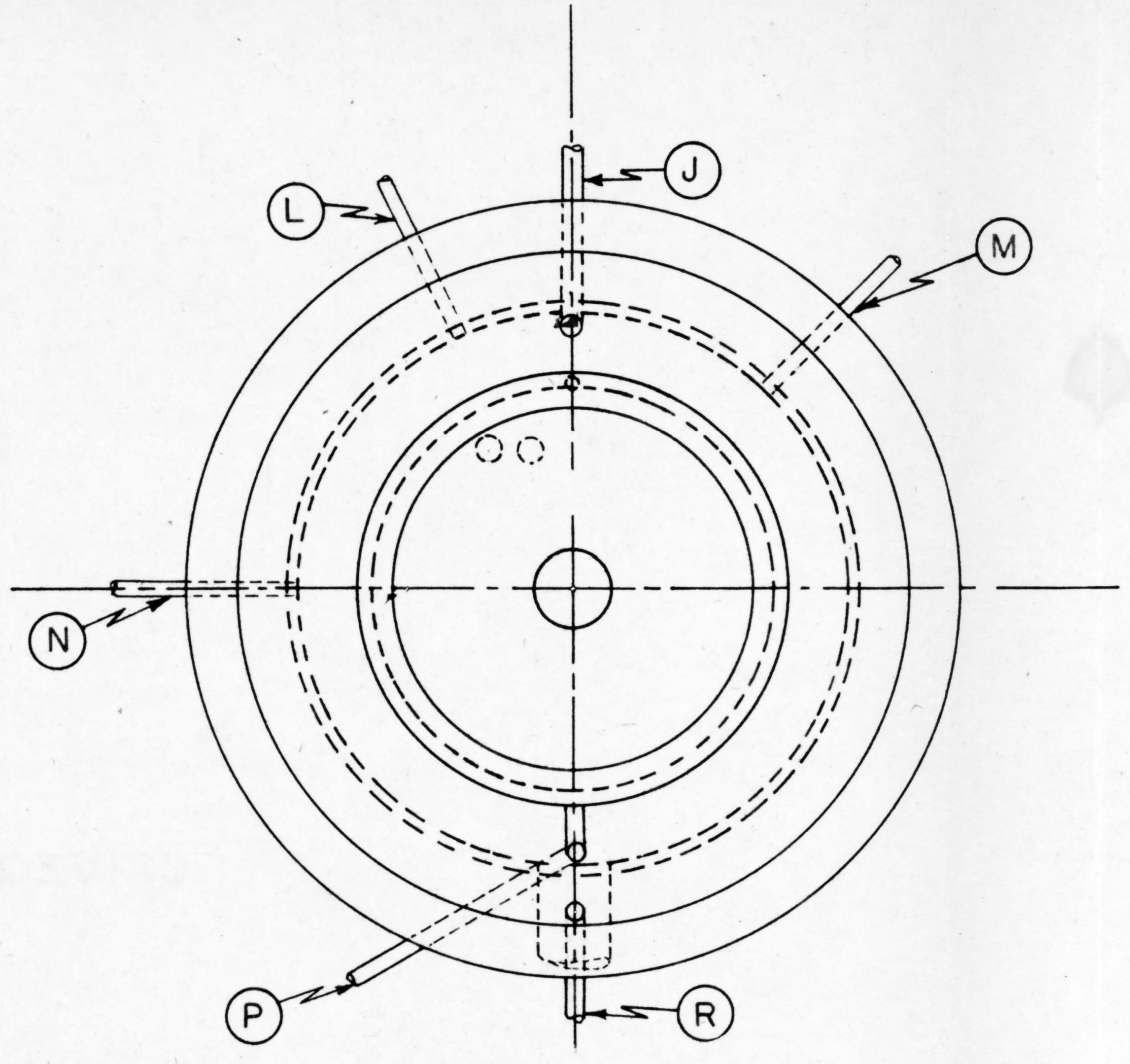
On the back of the base plate, the vacuum outlet to the McLeod gage, the feed inlet, the residue outlet, distillate-recycle and outlet lines were silver-soldered to the respective parts in the feed system. The feed thermocouple was inserted into the feed line and the residue thermocouple was inserted into the vacuum outlet line through the run of tees in the respective lines. The thermocouples were secured into place by compression-type fittings.

The vacuum system was connected to the base-plate connection for vacuum takeoff by a 37-inch length of 1-inch copper pipe as shown in Drawing 2, page 92.

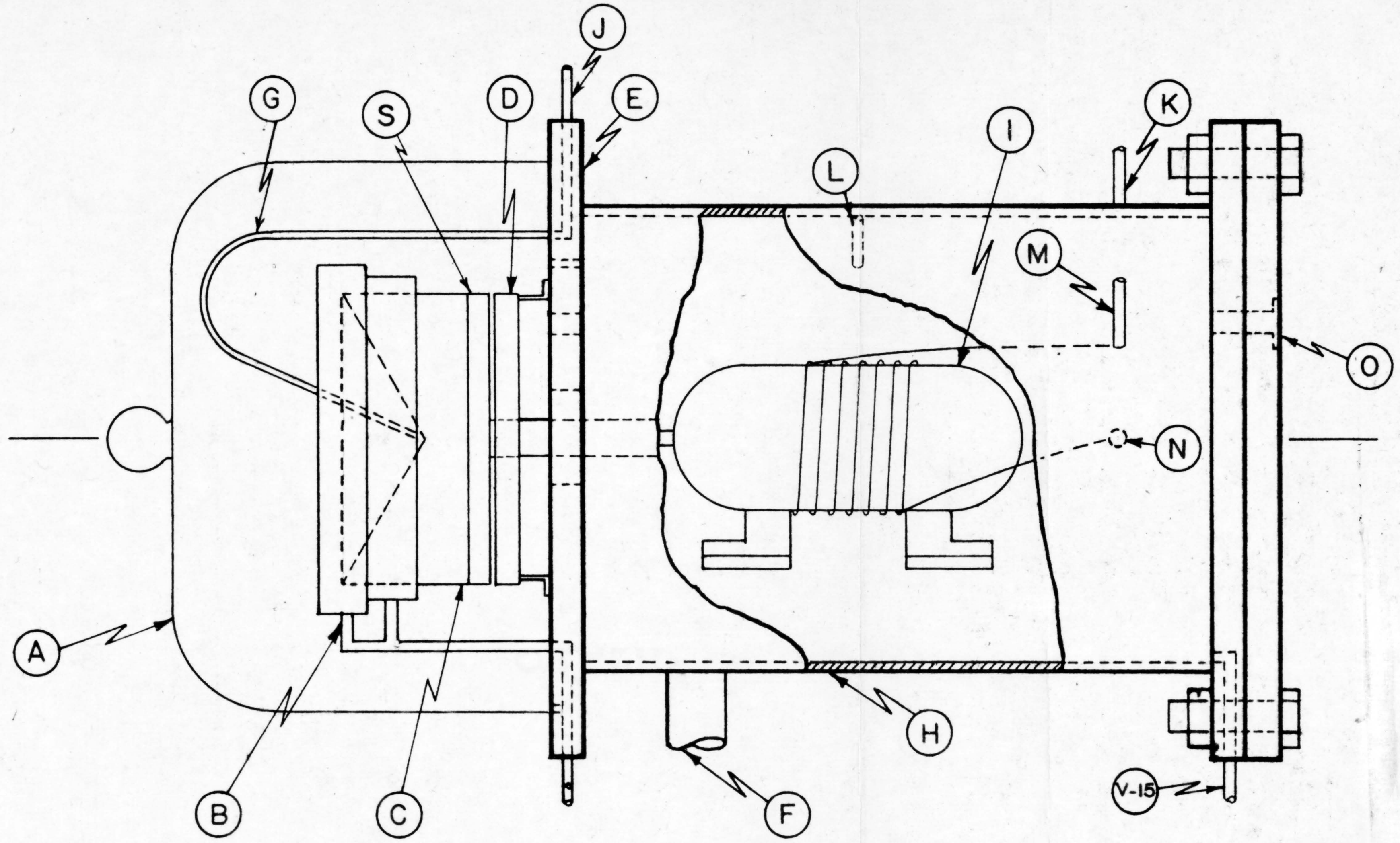
The rotor housing was assembled as follows: Garlock 926 Plastallic packing was packed into the housing around the shaft until 1-1/2 inches of packing-shaft contact resulted. The lantern ring was then inserted followed by 1-1/2 inch bronze spacer. The tightening nut was engaged with the housing, Andok B lubricant was applied to the shaft through the lubricant inlet, the drive motor was connected to the shaft by means of a flexible coupling, and the shaft was then rotated. The tightening nut was tightened slowly until the motor began to slow down appreciably. After the motor regained its original speed, the tightening nut was tightened again. This procedure was followed until the nut could be tightened no more. The tightening nut, the bronze spacer, and the lantern ring were removed from the housing, the length of compressed packing was measured, additional packing was added if the shaft-packing contact was not 1-1/2 inches and the above procedure was repeated. As soon as the proper amount of packing was formed into place, the lantern ring was inserted into place followed by sufficient packing to fill the housing. In like manner, with the aid of the tightening nut, this packing was compressed into place. The bearings and seals were tested by evacuating the system to observe if the desired vacuum could be obtained.

Modification of All-Metal Unit to Include Motor Drive Within Vacuum System. Since considerable difficulty was encountered in maintaining a vacuum-tight seal of the rotor despite the various modifications made to the rotor housing, the unit was redesigned and reconstructed to enclose the motor drive within the vacuum system. The new design necessitated several modifications of the still head assembly as used in the preliminary design; however, all accessory equipment and flow lines in the designed system remained intact as shown in Drawing 9, page 119.

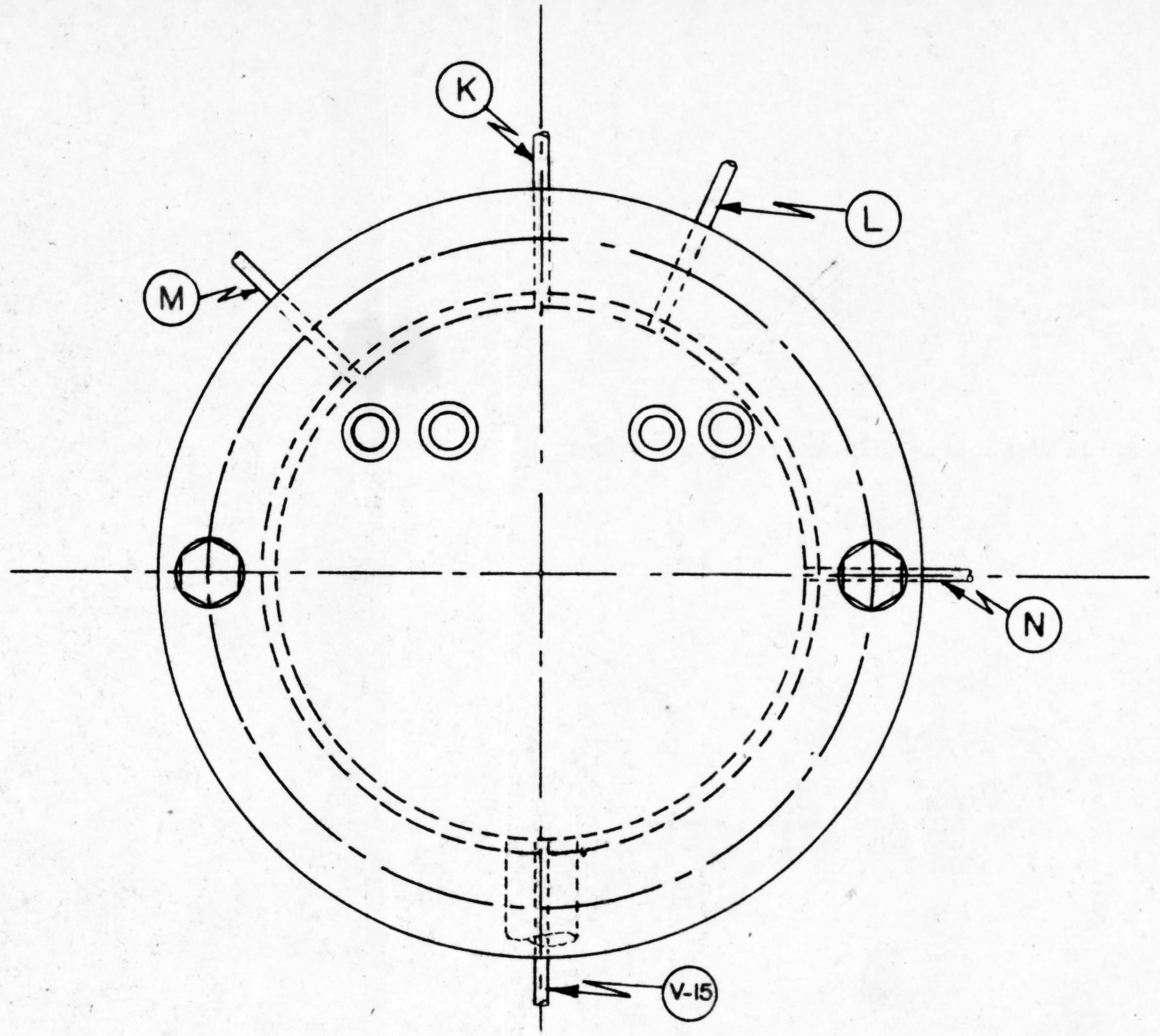
Modified Still Head Assembly. The major modifications involved only the still head assembly. The manner in which these modifications were included into the new design will be given under the appropriate headings that follow. For



FRONT ELEVATION



RIGHT SIDE ELEVATION



REAR ELEVATION

Ⓐ	BELL JAR
Ⓑ	DRAIN GUTTER
Ⓒ	ROTOR
Ⓓ	ROTOR HEATER
Ⓔ	BASE PLATE
Ⓕ	VACUUM PUMP CONNECTION
Ⓖ	FEED LINE
Ⓗ	VACUUM CHAMBER
Ⓘ	ROTOR MOTOR
Ⓙ	FEED LINE
Ⓚ	VACUUM GAGE CONNECTION
Ⓛ	RESIDUE THERMOCOUPLE
Ⓜ	COOLING WATER OUTLET (MOTOR)
Ⓝ	COOLING WATER INLET (MOTOR)
Ⓞ	SPARK PLUG SOCKETS
Ⓟ	RECYCLE LINE
Ⓡ	PRODUCT LINE
(V-15)	VACUUM CHAMBER DRAIN VALVE
Ⓢ	ROTOR PLATE

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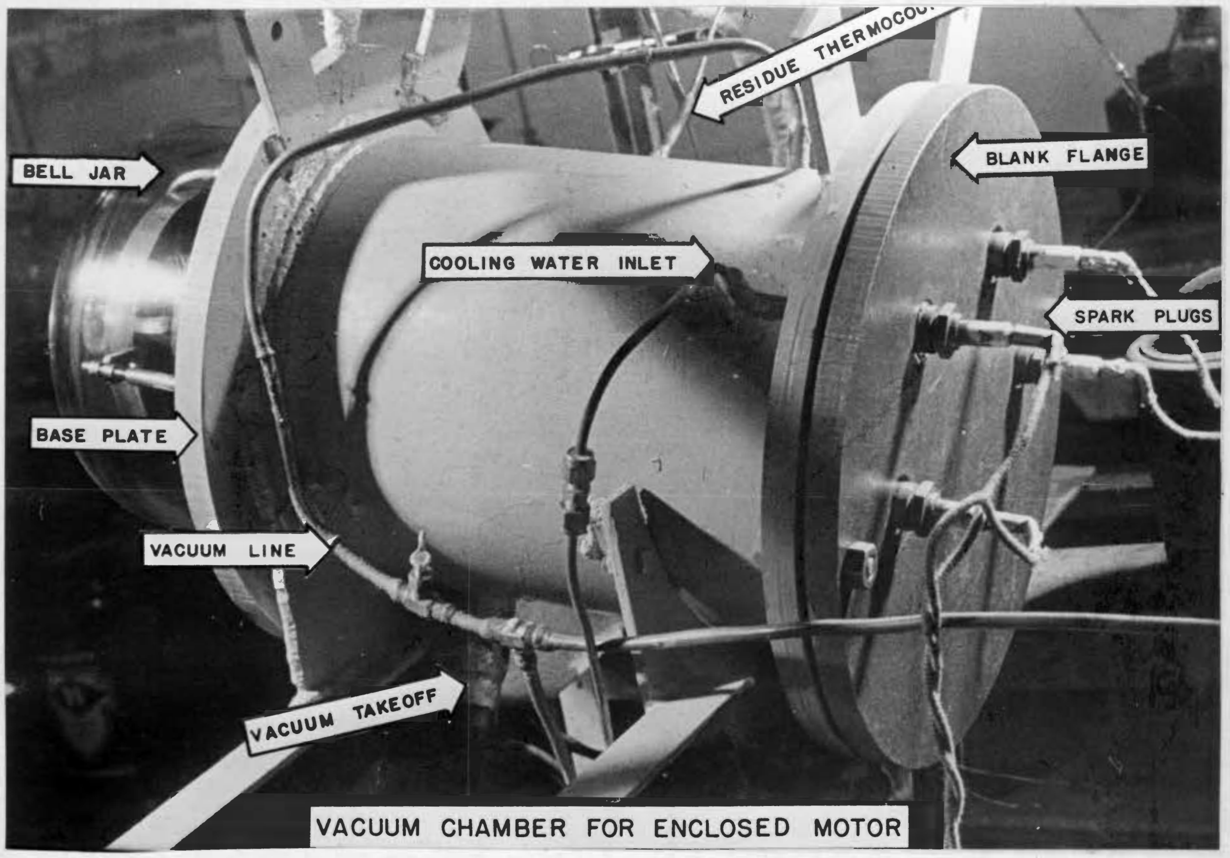
MODIFIED STILL HEAD ASSEMBLY IN VACUUM CHAMBER

SCALE: 3/8" = 1"	DATE	
DRAWN BY: DJS	4-1-53	CASE NO. 53
CHECKED BY: JWB	4-7-53	FILE NO. 799
APPROVED BY: [illegible]	4-7-53	DRAWING NO. 9



Photograph 4. Vacuum Chamber Assembly

purposes of clarity, attention is called to the features of the still head assembly that were not affected by the modification as well as the modification that were made.

Features of the Still Head Assembly Not Affected by the Modifications. The features of the still head assembly not affected by the modifications include the use of a steel base plate of the same dimensions with a groove in the face to accommodate the silicone gasket for the bell jar seal; the position of the feed inlet, residue and distillate draw-off connections on the face of the base plate; and the use of the same rotor, rotor plate, rotor heater, heater shell, and bell jar.

Modifications of the Still Head Assembly. Modifications in attachment of flow lines to base plate, construction and attachment of vacuum housing for motor drive to base plate, and the motor drive for the system, are described below and shown in Drawing 9, page 119.

Flow Lines into Base Plate. Holes, to accommodate the feed, distillate, and residue lines, were drilled into the periphery of the base plate midway between the front and back of the plate to meet the appropriate holes drilled into the face of the plate to accommodate the feed nozzle, gutter connection, and distillate draw-off. Three 1/8-inch iron pipe-to-tubing adapters, 2 inches long, were machined and threaded into the holes and then secured into place by bronzing. Three inch lengths of 1/4-inch copper tubing were silver-soldered into the adapters. A 3-inch hole was machined in the center of the base plate to serve as the vacuum outlet for the bell jar, to accommodate the rotor shaft, and to provide front access for tightening the motor support into place. A hole to accommodate a piece of 1/4-inch copper tubing was drilled into the base plate for the residue thermocouple. The tubing was bent and passed through the hole and secured to a sleeve in the vacuum housing. The residue thermocouple was then passed through and secured to the 1/4-inch copper tubing by a compression-type fitting which served to make a vacuum-tight seal.

Vacuum Housing for Rotor Motor Enclosure. The vacuum housing consisted of a piece of standard 8-inch iron pipe 11-1/2 inches long. Both ends of the pipe were machined for proper alignment, then beveled. A beveled groove, 1/4-inch oversize, was cut into the back of the base plate to accommodate the beveled end of the 8-inch pipe. The housing was secured to the base plate by electric welding, six overlapping beads served to make a vacuum-tight seal. A steel flange, 8-1/2 inches inside diameter by 12 inches outside diameter by 7/8-inch thick was machined and electric-welded flush with the other end of the housing. A circular groove, 8-1/4 inches inside diameter and 9-1/4 inches outside diameter and 1/8-inch deep was machined into the outer face of the flange to accommodate a silicone gasket for vacuum seal to the blank flange.

A steel blank flange, 12 inches outside diameter by 7/8-inch thick was machined, drilled and tapped to accommodate four No 45 AC spark plugs which served to connect the power supply to the rotor heater leads and the rotor motor leads through the flange and at the same time maintain a vacuum-tight seal. The spark plugs were prepared for assembly and placed into the flange as explained previously.

The housing was drilled to accommodate the following iron pipe adapters: McLeod gage connection on top side of the assembly 2 inches from the blank flange; the residue thermocouple inlet on the side of the assembly 4-1/4 inches from the back of the base plate; the vacuum connection to the diffusion pumps on the bottom side of the assembly 4 inches from the back of the base plate; and the inlet and outlet connections for cooling water to the coils surrounding the motor on each side of the assembly, 2-1/2 inches from the back flange. The adapters were secured to the housing by bronzing, then 2-inch lengths of copper tubing were secured to the adapters by silver-soldering for attachment to the proper connections in the still assembly.

Motor Drive for Rotor. The motor was wrapped with ten turns of 3/16-inch copper tubing through which water was circulated for cooling purposes. The motor was placed in the housing on a support, and after the motor shaft was aligned with the opening in the center of the base plate, the motor was bolted into place. The shaft, consisting of a 3-inch length of machine steel, 7/8-inch diameter, and drilled to accommodate a 1/2-inch diameter shaft was placed through the opening in the center of the base plate and slipped over and secured to the motor shaft by two 1/8-inch Allen-type set screws. The rotor plate was secured to the shaft by means of a 1/2-inch SAE nut and the rotor was secured to the plate as described previously on page 116.

Vacuum Pumping System. The vacuum pumping system, consisting of forepumps (megavacs), diffusion pumps, and a product tank evacuating pump, was assembled as follows:

Forepumps. Two megavacs, connected in parallel to an oil-diffusion pump, served as forepumps for the vacuum system. These pumps were connected to the diffusion pump by welded copper connections and 1/2-inch copper tubing.

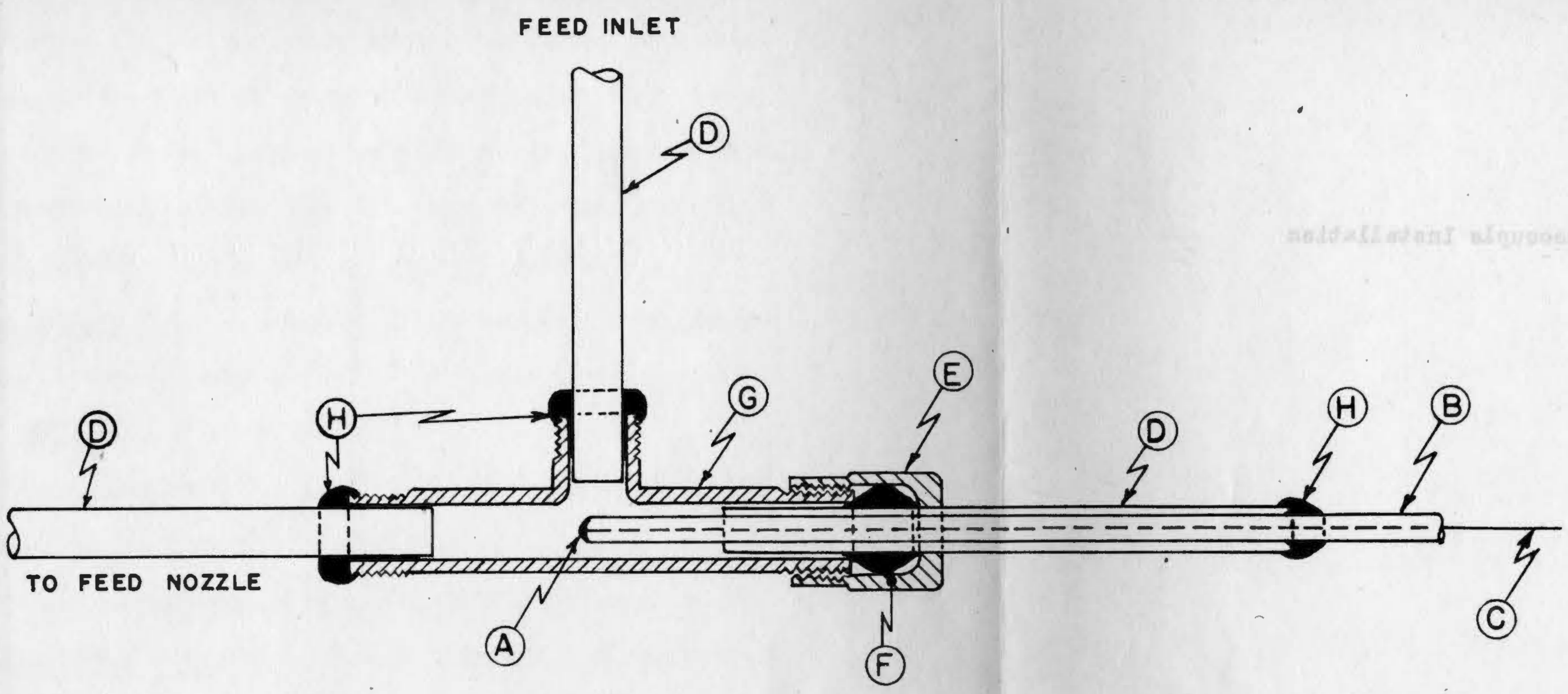
Diffusion Pumps. In a preliminary design, Drawing 1, page 91, two metal diffusion pumps, one horizontal, one vertical-type, were used in the system. The high-vacuum side of the horizontal pump was soldered to the vacuum outlet of the base plate. The high-vacuum side of the vertical pump was soldered to the exhaust side of the horizontal pump. The horizontal pump was the larger of the two, its oil capacity being 1500 milliliters compared to 500 milliliters for the vertical pump. With this arrangement of pumps, the system could be evacuated to 1 micron, absolute pressure. After several tests had been made, it was found that the horizontal pump was not functioning properly and a vacuum of better than 18 to 20 microns could not be obtained. The actuating oil was changed, heater connections were sealed and all joints were tested for leaks with vacuum grease with no improvement in the vacuum being obtained. Finally, all of the actuating oil (Amoil-S) was withdrawn from the horizontal pump and the vertical pump put into individual operation with a resulting pressure of 2 to 3 microns being obtained. As a result, the horizontal pump was replaced in the vacuum system by a second vertical pump, P, and water-cooled collection tank, R, Drawing 2, page 92. With the new assembly of two vertical diffusion pumps, the system could be evacuated to 1.5 microns of mercury, absolute pressure.

Product Tank Evacuating Pump. To be able to drain the product tank after the collection of each fraction of distillate, the tank had to be vented to the atmosphere. This necessiatated, of course, complete evacuation of the tank before it could be "cut back into" the vacuum system for the collection of the next fraction. Hence, a hyvac pump, M, Drawing 1, page 91, was connected directly to the tank for this purpose.

Heaters. The heaters used in the system consisted of a ring-type heater element for supplying the heat to the rotor, a flexible sheath heater for preheating the feed as it flowed from feed pump to the rotor, and heating tape heaters for preheating the feed tank and maintaining the temperature of the distillate tank at approximately 100 degrees Centigrade. The feed-line heater and the rotor heater remained "on" with varying amounts of voltage throughout any given test. The feed tank heater was used only for short periods at the beginning of each test to aid in keeping the large body of feed up to temperature. The distillate tank heater was also used throughout the test but with a constant voltage of about 1/3 of full-line voltage. This heater was used primarily to maintain the viscosity of the oil fractions low enough for good drainage from the bell jar to the distillate tank throughout the test.

Thermocouple Construction and Installation. In order to install thermocouples into the feed and residue lines and make a vacuum-tight seal, the following procedure was followed:

The copper-constantan thermocouples were made from a 24-inch lengths of 1/8-inch copper tubing and 36-inch lengths of Leeds and Northrup No 24 insulated constantan wire. The wire was inserted into the tubing and pushed through to the end. The copper tubing was peened around the wire and finally the tube and wire were fused together (oxy-acetylene flame) to form the thermocouple junction. A vacuum-tight connection for the installation of the thermocouples into the system was made as shown in Drawing 10, page 128. In order to secure the 1/8-inch tubing into the 1/4-inch



LEGEND

Ⓐ	COPPER-CONSTANTAN THERMOCOUPLE JUNCTION
Ⓑ	$\frac{3}{4}$ INCH COPPER TUBING - COPPER LEAD
Ⓒ	INSULATED CONSTANTAN WIRE - CONSTANTAN LEAD
Ⓓ	$\frac{1}{4}$ INCH COPPER TUBING
Ⓔ	COMPRESSION SCREWED FITTING
Ⓕ	FERRULE
Ⓖ	$\frac{1}{4}$ INCH STANDARD BRASS TEE DRILLED TO ACCOMMODATE $\frac{1}{4}$ INCH TUBING AS SHOWN
Ⓗ	SILVER - SOLDERED CONNECTIONS

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

FEED THERMOCOUPLE
INSTALLATION

SCALE: NONE DATE	
DRAWN BY: [illegible] 1-12-53	CASE NO. 53
CHECKED BY: [illegible] 1/13/53	FILE NO. 799
APPROVED BY: [illegible] 1/14/53	DRAWING NO. 10

tee connection, it was necessary to solder a collar of 1/4-inch tubing around the 1/8-inch tubing and then secure the 1/4-inch collar in place in the 1/4-inch tee by a compression-type fitting. This type of connection allowed for the ready removal of the thermocouples for inspection and repair of the system.

Preliminary Tests. The preliminary tests included attempts to prepare a constant-yield oil in a standard laboratory distillation unit, decolorization tests on various oils for the preparation of a colorless oil for use in the feed mixtures, and the calibration of the feed and residue thermocouples.

Constant-Yield Oil Preparation in a Standard Laboratory Distillation Unit. A laboratory, vacuum-distilling assembly consisting of a 5-liter, three-neck flask heated by a glascol heater, a water-cooled condenser, a thermometer, a product collection flask, and a hyvac vacuum pump was used in the preliminary attempts to prepare a constant-yield oil from light grade mineral oil. A vacuum of 27-1/2 inches of mercury, referred to a 28-inch barometer reading, was maintained in the system throughout the tests. The initial boiling point of the oil at this pressure was 180 degrees Centigrade. Attempts were made to collect the distillate fractions at 10 degree Centigrade increments, starting at 180 degrees Centigrade. For the collection of each fraction, the temperature was increased at the rate of approximately one degree per minute to the maximum for the particular fraction, collecting the distillate during the temperature rise and until all of the particular fraction had been distilled over at the maximum temperature for the fraction. The method proved unsatisfactory because of apparent pyrolysis of the feed and the production of an off-color distillate. The first two or three fractions were easily obtained, but when the feed was heated above 210 degrees Centigrade, violent boiling and foaming occurred necessitating the lowering of the temperature. After the batch had cooled as much as 30 or 40 degrees, distillate could still be collected even though fractions at these temperatures had previously been completely collected. It was apparent that a satisfactory constant-yield oil could not be prepared by this manner. It was therefore decide to dispense with this method and make the constant-yield oil in the molecular still.

Decolorization Tests. Since a colorimetric method was to be used in the analysis of the distillate fractions, a colorless or nearly colorless oil was desired for preparation of the constant-yield oil. Attempts were made to decolorize Essolube No 7 motor oil for use as a high boiling component in the preparation of a constant-yield oil by heating the oil in the presence of decolorizing carbon and then removing the carbon by filtration. Tests were made on equal volumes (100 milliliters each) of the oil and decolorizing carbon, heated to temperatures of 100, 150, 200, 225, and 250 degrees Centigrade, agitated by hand-stirring with a bent glass stirring rod during the heatup period and during the 30-minute "soaking" period prior to filtration. The filtrates obtained from all of the tests were somewhat lighter in color than the original oil, but not sufficiently improved in color for use in the preparation of constant-yield oil. The increase in temperature and added times of exposure to decolorizing carbon had no visual effect on the color of the product obtained, all being light orange-yellow in color.

Teresso 52 and Cenco hyvac oil were also tested in a similar manner with no significant improvement in color. The decolorizing tests were then dispensed with and colorless light, heavy, and extra heavy grades of mineral oil were used in attempts to prepare a constant-yield oil.

Thermocouple Calibration. The cold junction of the two copper-constantan thermocouples were connected to a double-pole, single-throw switch which was in turn connected to a Fisher type S potentiometer. The thermocouples were calibrated by placing the bead of each in a oil bath together with a standard thermometer and an electric stirrer. The oil bath was agitated and heated at the rate of 0.5 degree per minute. Potentiometer readings for both thermocouples were made after each five-degree temperature increase from 50 to 225 degrees Centigrade. A calibration curve was made of the potentiometer readings versus the temperatures for each thermocouple.

Operational Procedure. Since the performance of the molecular still depends on the operating variables of distillation, it was necessary to develop a technique of operation whereby results could be duplicated. Accordingly, two techniques were evolved which will be referred to as the continuous technique and the discontinuous technique of collecting distillate fractions.

In the continuous technique of operation, the distillate was collected continuously during each of the temperature increments. In the discontinuous technique, however, the distillate was collected for a definite period of time only at the upper limit of the fraction temperature with both residue and distillate being recycled until the desired feed and residue temperatures had been obtained. Since the latter technique proved the more favorable for control purposes and was adopted as the method of collecting the distillate fractions, it will be described in detail. A brief description of the continuous technique will also be given.

Operation of the Still Using the Discontinuous Technique of Collecting Distillate Fractions. Before the actual operational test procedure to obtain data for the elimination curves could be started, the vacuum system had to be sealed and placed into operation, the feed had to be prepared and added to the feed tank and given a preliminary heating and degassing period, and the thermocouple cold junction had to be made ready and the potentiometer balanced. After the test had been completed, the system had to be shut down and cleaned and made ready for the subsequent tests. In describing the procedure, reference is made to the modified piping diagram, Drawing 2, page 92, unless otherwise noted.

Feed Preparation. From a number of preliminary tests, it was found that when 7 volumes of light grade mineral oil and 8 volumes of heavy grade mineral oil were mixed together and distilled in the molecular still, according to the technique to be described, a nearly constant-yield oil was obtained. Since the operating capacity of the feed tank of the still was approximately 800 milliliters, the volume of feed oil did not in any case exceed 750 milliliters. For a feed volume of 750 milliliters, 350 milliliters of light mineral oil was added to 400 milliliters of heavy mineral oil. The oil was placed in a Waring blender and a known weight of dye was added. The plastic lid was placed on the blender and the agitator motor turned "on". The dye was completely dissolved in the oil after 30 minutes of agitation. At least 20 milliliters of the oil-dye feed mixture was removed from the blender and reserved for colorimetric analysis; the remainder of the batch constituting the feed mixture for the molecular still.

McLeod Gage. The hyvac pump used to operate the McLeod gage was turned "on" as the first step in readying the system for operation. The gage was opened to the pump to allow the mercury in the gage reservoir to be relieved of any oil vapors from a previous test and to prevent surges of mercury in the gage when the still was evacuated. This degassing of the mercury required at least 30 minutes before the gage would operate properly.

Still Proper. In readying the still for operation the following valves were closed: V-1, V-2, V-4, V-8, V-9, V-10, V-12, and V-14. All the other valves in the system, V-3, V-5, V-6, V-7, V-11, and V-13 were opened. The silicone gasket, D, Drawing 1, page 91, was placed in position in the groove of the base plate provided for it and the bell jar was then centered on the gasket. The bell jar was pressed firmly against the gasket and the two megavacs turned "on". As soon as the pressure in the system was lowered sufficiently to hold the bell jar in position, the safety strap, Y, Drawing 1, page 91, was secured into place. The McLeod gage was observed at all times during this initial startup and the backing pressure to the gage was balanced against the system to prevent mercury from being drawn from the gage into the flow lines of the still.

An approximate indication of the pressure in the system could be gained from the characteristic sounds of the megavac pumps. Initially, the valves of the pumps have a muffled sound, but as the pressure decreases, the sound becomes more metallic and at a backing pressure of 200 microns or less, the sound has a characteristic metallic click. Once the operator has become accustomed to the operating sounds, he does not have to measure the pressure on the McLeod gage until after the clicking sound has developed. Occasional readings on the gage should then be taken to ascertain the progress of the pumps in degassing the system and the Amoil-S oil in the diffusion pumps.

Addition of Feed to Still. To aid in expediting the distillation, the oil-dye mixture was preheated to 100 degrees Centigrade in a beaker placed on a hot plate while the system was being evacuated. When the McLeod gage indicated an absolute pressure of 100 microns or less in the system, the loading tank, U, was filled with the hot feed mixture, and valve V-2 was opened slightly to allow the feed to enter the feed tank, S. A level was maintained in the loading tank by continual addition of feed mixture from the beaker and regulation of valve V-2. As soon as the beaker was emptied and the level of the oil in the loading tank reached the opening of the tube connecting the loading to the feed tank, valve V-2 was closed. By this procedure, the vacuum was not lost in the system, and only 2 to 3 milliliters were left in the loading line.

Heating and Degassing. The electric current was turned "on" to the powerstat controlling the current to the rotor heater, D, and preheater, W. Initially, the voltage input to the rotor heater was adjusted to about 60 volts while that to the preheater was about 35 volts. Feed pump, N, was put into operation by applying current to the field coil actuating the pump plunger. The feed rate was adjusted to the smoothest flow possible by raising or lowering the field coil relative to the pump body. The actual feed rate was unimportant at this point since this was primarily a preheating and degassing period in the operation. Next, the motor operating the rotor was turned "on" and adjusted to the desired speed by powerstat control. As the feed increased in temperature at about one degree Centigrade per minute and passed over the revolving rotor in a thin film, the degassing operation was enhanced. When the absolute pressure in the system was below 50 microns absolute pressure, the diffusion pumps, P and Q, were placed into operation by plugging the leads of the heater elements into a 115-volt socket. Immediately, cooling water was turned "on" to the cooling coils surrounding the bodies of the diffusion pumps. An increase in pressure to approximately 150 microns was noted as soon as the oil in the diffusion pumps became heated because of further removal of dissolved gases from the Amoil-S diffusion pump oil. If the system were functioning properly, this increase in pressure persisted only about 15 minutes after which the pressure decreased to 1 to 2 microns in approximately 10 to 15 minutes.

Product Tank Evacuation. The vacuum pump used to evacuate the product tank, Z, was turned "on" so that the tank would be at the same or nearly the same pressure level as the system when it became time to withdraw a sample of distillate.

Calibration of Feed Pump. Distillate fractions were collected for the same contact time of feed with rotor for each fraction at a constant feed rate. The time of contact of the feed with the rotor was expressed as the nominal number of passes of the total feed across the rotor and required the determination of the feed rate. Since the flow of oil through the flow system was affected greatly by the change in viscosity with temperature increases and by the removal of the various fractions throughout a test, it was necessary to adjust the feed rate to the desired constant value before taking each fraction. The determination of the feed rate was made at 2 to 3 degrees Centigrade below the particular fraction temperature. Valve V-3 was closed and the time noted for the pump to remove all the feed, as observed by no further feeding to the rotor, from tank S. Any of the constituents of the feed that might have distilled in passing over the rotor were condensed and also returned to top tank T through the by-pass line shown with V-7 open.

The hold-up of feed in the flow lines was found to be approximately 50 milliliters and this correction was applied in calculating the average flow rate per minute. In the event that the feed rate was found to be too fast or too slow, adjustments were made by raising or lowering the field coil controlling the length of the stroke of the pump plunger.

Collection of Distillate Fraction. As soon as the proper feed rate was established, the temperature of the residue was increased to the fraction collection temperature by increasing current input to the rotor heater and the feed preheater, the feed temperature being maintained approximately 10 degrees Centigrade below that of the residue temperature to avoid flashing of the feed as it fed from the nozzle which would cause splashing. Valve V-7 was closed, valve V-8 was opened and the feed passed across the rotor for the calculated time for a given number of passes. At the end of the specified time, valve V-7 was opened and valve V-8 was closed, in that order, to minimize drainage error. The current to the rotor heater and preheater was increased immediately after taking the fraction in preparation for taking the next higher fraction. The distillate sample in tank Z was removed by closing valve V-11, venting the tank to the atmosphere by opening valve V-10, and then opening valve V-12, and the volume measured. After the distillate was removed from the tank, the tank was readied for the next fraction by closing valves V-10 and V-12, opening valve V-11, and allowing the pump to evacuate the tank during the time that the feed was being heated to the next collection temperature.

"Shutdown" of Still. As soon as the final distillate fraction was collected, the power to the diffusion pump heaters, the rotor heater, the feed preheater, the feed pump, the rotor motor, and the hyvac pump used to evacuate the product tank was turned "off". The rest of the system remained as before under the vacuum produced by the megavac pumps alone for at least 45 minutes to allow the diffusion pump oil to cool in order to prevent pyrolysis of the oil. After the oil had cooled, the power to the megavac pumps was turned "off" and the system vented to the atmosphere by opening valves V-8 and V-10. As soon as the system was vented to the atmosphere, the hyvac pump used to operate the McLeod gage and the cooling water to the diffusion pumps were turned "off".

Cleaning of the Still for Subsequent Test. The bell jar was removed and the residue remaining in the feed tank S was drained by opening valve V-1. The cold trap, R, was drained of any condensate by opening valve V-14. As soon as drainage was complete, valves V-1 and V-14 were closed and approximately 250 milliliters of light grade mineral oil, preheated to 100 degrees Centigrade, were added to the feed tank, S, through the loading tank, U, to be used to flush the flow lines. The oil was pumped through the flow lines and tanks for at least five minutes, after which the operation of the feed pump was stopped and the wash oil allowed to drain from the system through valves V-1 and V-12. The system was washed at least three times using this procedure. After the drainage of the final wash oil, compressed air was blown through the flow lines to aid in more complete drainage especially of the oil trapped in the feed pump. The system was then considered clean and ready for the next test.

Operational Instructions. Detailed instructions of operation are presented to enable future investigators to extend the scope of the work already begun. The preparation of the feed, operating procedure using the discontinuous technique of collecting distillate fractions, "shutdown" and cleaning of the still for subsequent tests are described step by step. The following represents the operating instructions to be adhered to in distillations using the molecular still with reference made to Drawing 2, page 92, unless otherwise noted:

Preparation of Feed for Molecular Still:

1. Measure 350 milliliters of light and 400 milliliters of heavy mineral oils into a liter graduated cylinder.

2. Pour contents of graduated cylinder into Waring blendor.

3. Place plastic cover on blendor and agitate mixture for 1 minute.

4. Weigh out desired amount of dye and add to oil in blendor.

5. Agitate mixture for 30 minutes to completely dissolve dye (Note: Do not operate blendor more than 15 minutes out of every 45 minutes).

6. Remove 30 milliliters of oil-dye mixture from blendor and save for colorimeter analysis. The remaining 720 milliliters of the mixture constitute the feed for the still. Transfer this volume to a one-liter beaker and heat to 100 degrees Centigrade on a hot plate while the still is being made ready for operation.

Still Operation - Start-up Procedure and Preliminary Operation:

1. Turn "on" hyvac pump used to operate McLeod gage.

2. Open gage to pump and allow mercury in reservoir of gage to be relieved of any gas or vapors from a previous test.

3. Close valves V-1, V-2, V-4, V-8, V-9, V-10, V-12, and V-14.

4. Open valves V-3, V-5, V-6, V-7, V-11, and V-13.

5. Place silicone gasket, D, Drawing 1, page 91, in position in groove on face of base plate.

6. Center bell jar on gasket and press firmly against the gasket.

7. Turn "on" both megavac pumps.

8. Secure safety strap, Y, to bell jar as soon as the pressure in the system is lowered sufficiently to hold the bell jar in place.

9. Observe McLeod gage at all times during the initial start-up and be sure that the backing pressure and head of mercury in the gage is greater than absolute pressure in the system to prevent mercury from being drawn from the gage to the flow lines of the still.

10. Add preheated feed mixture to feed tank, S, through loading tank, U, as soon as the absolute pressure in the still becomes 100 microns or less. (Note: If system is vacuum-tight, an absolute pressure of 100 microns or less should be obtained in 30 to 45 minutes). The feed is added to the system in the following manner:

    a. Fill loading tank, U, with feed mixture.

    b. Open valve V-2 slightly to allow feed to flow to feed tank, S.

    c. Maintain liquid level in loading tank by continual addition of feed mixture from beaker and regulation of valve V-2.

    d. Close valve V-2 when beaker is emptied and liquid level in loading tank reaches the mouth of the tube connecting the loading and feed tanks.

11. Turn "on" electric power to powerstat controlling the voltage to the rotor heater, D, and feed preheater, W.

12. Adjust the voltage to the rotor heater to 60 volts and the voltage to the feed preheater to 35 volts.

13. Place feed pump, N, into operation by applying current to field coil actuating the pump plunger.

14. Adjust the feed rate to the smoothest flow possible by raising or lowering the field coil relative to the pump body. (Note: For preheating and degassing period only).

15. Turn "on" power to the powerstat controlling the voltage to the rotor motor adjust to proper speed of rotation by powerstat control.

16. Turn "on" cooling water to cooling coils surrounding the body of the rotor motor.

17. Turn "on" cooling water to cooling coils surrounding the bodies of the diffusion pumps.

18. Turn "on" power (115 volts) to diffusion pump heaters as soon as the absolute pressure in the system is 50 microns or less. (Note: Within 2 or 3 minutes after the diffusion pump heaters are turned "on", the pressure in the system will increase to approximately 150 to 250 microns because of release of dissolved gases from diffusion pump oil. This increase in pressure will persist for 5 to 10 minutes after which the absolute pressure will decrease to 1 to 2 microns (6 microns in later tests) in about 15 minutes total elapsed time after applying power to the heaters.)

19. Turn "on" hyvac pump used to evacuate product tank, <u>Z</u>.

20. Place crushed ice in thermos bottle for thermocouple cold junction.

21. Balance potentiometer.

22. Determine the feed rate of pump approximately 2 or 3 degrees Centigrade below the desired fraction collection temperature and adjust to the desired feed rate. Feed Rate is determined as follows:

    a. Close valve <u>V-3</u>, note time.

    b. Observe time when feed from feed nozzle stops.

    c. Open valve <u>V-3</u>. (Note: Holdup in flow lines measured to be 50 milliliters.)

    d. Calculate average feed rate on basis of volume of feed in system minus holdup volume of 50 milliliters.

e. If feed rate is determined to be too fast or too slow, adjust stroke of plunger by raising or lowering the field coil and repeat above procedure until the desired feed rate is obtained.

Still Operation - Distillate Collection:

1. Obtain desired feed rate.

2. Check rotor speed with Strobotac and adjust powerstat if necessary.

3. Increase residue temperature to fraction collection temperature by increasing current input to rotor heater and feed preheater when necessary. (Note: To avoid splashing of the feed as it issues from the feed nozzle onto the rotor, maintain the feed temperature at least 7 to 10 degrees Centigrade below the residue temperature at all times).

4. Close valve V-7, note time.

5. Open valve V-8, to collect distillate.

6. Allow feed to flow over rotor for calculated time for the given nominal number of passes.

7. Open valve V-7 at end of calculated time period.

8. Close valve V-8.

9. Increase voltage to rotor heater and feed preheater in preparation for taking next fraction.

Still Operation - Removal of Distillate from Tank Z:

1. Close valve V-11.

2. Open valve V-10 to vent tank to atmosphere.

3. Place receiver beneath tank outlet and open valve V-12. Collect distillate and measure volume.

4. Close valves V-10 and V-12.

5. Open valve V-11 and allow hyvac pump to evacuate tank Z until it is needed to collect next fraction.

6. The distillate collection and removal procedures are repeated for each fraction collection.

Still Operation - Shutdown Procedure:

1. Turn "off" power to the diffusion pump heaters, rotor heater, feed preheater, feed pump, rotor motor, and hyvac pump used to evacuate the product tank.

2. Allow remainder of system to continue under vacuum for 45 minutes to permit the diffusion pump oil to cool before venting to the atmosphere.

3. Turn "off" power to the megavac forepumps.

4. Open valves V-8 and V-10 to vent system to the atmosphere.

5. Turn "off" cooling water to cooling coils surrounding the diffusion pumps and to cooling coils surrounding the rotor motor.

Cleaning of Still:

1. Remove safety strap, Y, from bell jar.

2. Remove bell jar and wipe inside of jar with clean rag wetted with benzene.

3. Open valve V-1 to drain residue from feed tank S.

4. Open valve V-15 (Drawing 9, page 119) to drain vacuum housing.

5. Open valve V-14 to drain cold trap R.

6. Close valves V-1, V-14, and V-15.

7. Add approximately 250 milliliters of light mineral oil, preheated to 100 degrees Centigrade, to the feed tank, S, through loading tank, U.

8. Turn "on" feed pump and allow wash oil to circulate through flow lines for 5 minutes.
9. Turn "off" feed pump.
10. Open valves V-1 and V-12, and drain wash oil from system and discard.
11. Repeat above procedure for flushing system at least three times.
12. Blow compressed air through system after last wash for 2 or 3 minutes to aid in the removal of any oil trapped in the feed pump and flow lines.
13. System is now ready for next test.

Operational Procedure Using the Continuous Temperature Rise Technique of Collecting Distillate Fractions. The over-all operational procedure using the continuous temperature rise technique of collecting distillate fractions was identical with that just described except for the fraction collection. As soon as the still was placed into operation and heat was applied to the feed preheater and rotor heater, valve V-7 was closed and valve V-8 was opened. All of the distillate that would distill was collected during the time interval of heating the feed and residue through the range of temperature for each fraction. As soon as the residue temperature corresponded to the end temperature of a desired fraction (100 degrees Centigrade for the 90 to 100-degree temperature fraction, for instance), valve V-8 was closed ending the collection of this fraction. The distillate of the subsequent fraction was allowed to collect in the bell jar until the distillate tank, Z, could be vented (valve V-9 closed, valve V-10 opened); drained (valve V-12 opened); re-evacuated (valves V-12 and V-10 closed and valve V-11 opened); and placed back into the system (valve V-11 closed, valves V-9 and V-8 opened) allowing the distillate fraction once more to flow to the distillate tank, Z. This procedure was followed for collecting the distillate fraction for each 10-degree Centigrade rise in temperature from 100 to 180 degrees Centigrade. Attempts were made to increase the voltage input to the heaters at about the same rate from test to test in order to maintain a constant distilling time interval for each fraction, but variable line voltage made this impossible. Accordingly, this continuous temperature rise technique was discarded in favor of the discontinuous temperature rise technique.

Preparation of Constant-Yield Oil. Attempts to prepare a constant-yield oil by preliminary distillation of the light and heavy grades of mineral oil in a laboratory pot still under vacuum proved unsatisfactory because of pyrolysis of the oil. The mineral oil was then distilled in the molecular still using the continuous temperature rise technique of collecting distillate fractions. Equal volumes of the various fractions were combined to give a constant-yield oil and 400 milliliters of this blended mixture were distilled to ascertain the constancy of the yields. The blended mixture did not prove to be a satisfactory constant-yield oil. In fact, a more constant-yield oil could be obtained by the blending of 7 volumes of light mineral oil with 8 volumes of heavy mineral oil. Blended mixtures of this proportion were employed as the constant yield oil for the carrier oil in the dye distillations (later reduced to 300 milliliters of light mineral oil to 350 milliliters of heavy mineral oil, a 6:7 volume ratio, for the standardized technique.)

Distillation of Mineral Oil Mixture for Colorimeter Blanks. A mixture of 350 milliliters of light mineral oil and 400 milliliters of heavy mineral oil was distilled to obtain fractions for use as colorimeter blanks. The distillation conditions were similar to those employed in the standardized technique of operation.

Distillation of Single Anthraquinone Dyes. Three dyes, 1,4-diethyldiaminoanthraquinone, 1,4-diisopropyldiaminoanthraquinone, and 1,4-dibutyldiaminoanthraquinone were distilled using the continuous temperature rise technique. Three dyes were also distilled using the discontinuous temperature rise technique with five nominal passes of the feed over the rotor; celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone. The three dyes used in the binary mixture distillations; celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone, were distilled individually using the standardized technique and operating conditions, which were as follows: (1) distillation pressure of 6 - 1 microns, (2) feed rate of 65 - 2 milliliters per minute, (3) rotor speed of 2000 - 50 revolutions per minute, (4) a 10-degree Centigrade difference between the feed and residue temperatures, and (5) two nominal passes of the feed over the rotor.

Distillation of Binary Mixtures of Dyes. Binary mixtures in weight ratios of 2:1, 1:1, and 1:2-1/2 of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone and binary mixtures of equal weight ratios of celanthrene red 3B and 2,6-dimethyldiaminoanthraquinone and 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone were distilled using the standardized technique with conditions as given previously.

Separation of Binary Mixtures by Molecular Distillation.

Tests were made to determine the feasibility of separating binary mixtures by molecular distillation. Two methods of separation were investigated. In the first method, referred to as extractive molecular distillation, the cumulative volumes of the distillates collected at 100, 110, 120, 130, and 140 degrees Centigrade from the distillation of a binary mixture of a 2:1 weight ratio of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone were used. The volume of these fractions used was 260 milliliters to which was added 340 milliliters of heavy mineral oil. This mixture constituted the feed for the extractive molecular distillation and was distilled under the same conditions as the original distillation.

In the second method, no additional mineral oil was added to the cumulative volumes of the 100, 110, 120, 130, and 140-degree Centigrade fractions. Instead, two duplicate batches of a 1:1 weight ratio of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone were prepared and distilled, and the cumulative volumes of the fractions through the 140-degree fraction were redistilled under identical conditions as in the original distillations. The cumulative volumes from the redistillation through the 140-degree fraction were redistilled for a second time.

The fractions obtained from all original distillations and subsequent redistillations for both methods were analyzed using the colorimeter to determine the dye concentration of each fraction.

Distillation of a Tertiary Mixture of Dyes. A tertiary mixture consisting of equal weights of each of the three dyes used in the tests on binary mixtures; celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone; was distilled again using the standardized technique. The fractions were analyzed colorimetrically as before to determine the dye concentration in each.

Analysis Procedure. The procedures followed in the calibration and in the analysis of the constant-yield oil and the dye distilland and distillate fractions are presented below.

Constant-Yield Oil. The fractional cuts of the constant yield oil prepared at 10-degree Centigrade temperature increments from 90 to 190 degrees Centigrade were comparatively analyzed by the use of a Klett-Summerson colorimeter.

Colorimeter Analysis. Since it was noted that the colorimeter reading for the clear, light and heavy mineral oils varied considerably, it was deemed necessary to zero or blank the colorimeter for each constant-yield oil fraction by the determination of the colorimeter reading of each fraction as compared to zero for light mineral oil. This data of the colorimeter readings of the various oil fractions versus the temperature of distillation was plotted and readings from the curve used to correct the colorimeter during dye analysis of the respective fractions.

Calibration of the Colorimeter with Dye Standards. Analysis by colorimetric means afforded a simple, rapid analysis of colored complex compounds. The determination of dye concentration in oil solutions required the establishment of standard curves for colorimeter readings versus the dye concentration. A known weight of the appropriate dye, approximately 0.0200 gram, was added to 100 milliliters of light mineral oil and agitated in a Waring blendor. Ten milliliter samples of the oil-dye mixture were taken after every 15 minutes of agitation for colorimetric determinations. The agitation was continued until two samples, taken 15 minutes apart, gave identical colorimeter readings. None of the dyes required more than one hour of agitation for complete solution. The sample of dye thus prepared was taken as the base standard and the other standards prepared therefrom by dilution of aliquot portions of the base standard and each succeeding standard with light mineral oil. For each colorimetric reading of these standards, the colorimeter was blanked against light mineral oil. The data obtained from the above procedure were used to plot colorimeter calibration curves for dye concentrations in grams of dye per 100 milliliters of solution. Calibration curves for each dye were made with each of the green, red, and blue filters for use in analyzing binary and tertiary mixtures of dyes.

Dye Analysis. The analysis of the feed and distillate products of single-dye distillations was performed according to standard colorimeter procedure. Each fraction was blanked against the corresponding fraction of constant-yield oil as explained previously.

The analysis of binary and tertiary mixtures of dyes required a more complex procedure. For purposes of explaining the procedure used, a hypothetical case of a mixture of a red and blue dye will be described. Figure 10, page , shows calibration curves of the two individual hypothetical dyes with red and blue filters. Suppose the mixture gives a colorimeter reading of 100 with the red filter, and since the red filter removes the effect of the red dye completely, the concentration of the blue dye in the mixture, C_B, can be determined from Curve A. The use of the blue filter then permits the determination of the concentration of the red dye in the mixture, C_R, by taking advantage of the additive properties of the calibration curves of the blue dye with the blue filter, Curve B, and the red dye with the blue filter, Curve C. Having determined the concentration of the blue dye, C_B, from Curve A, one can establish from Curve B, the colorimeter reading that concentration of blue dye, C_B, would give in solution alone, say 150. Subtraction of this reading, 150, from the colorimeter reading obtained on the mixture in question with the blue filter, say 350, gives a reading of 200 that is equivalent to the effect of the red dye alone with the blue filter. This equivalent colorimeter reading, 200, can now be used to determine the concentration of red dye, C_R, from Curve C as shown.

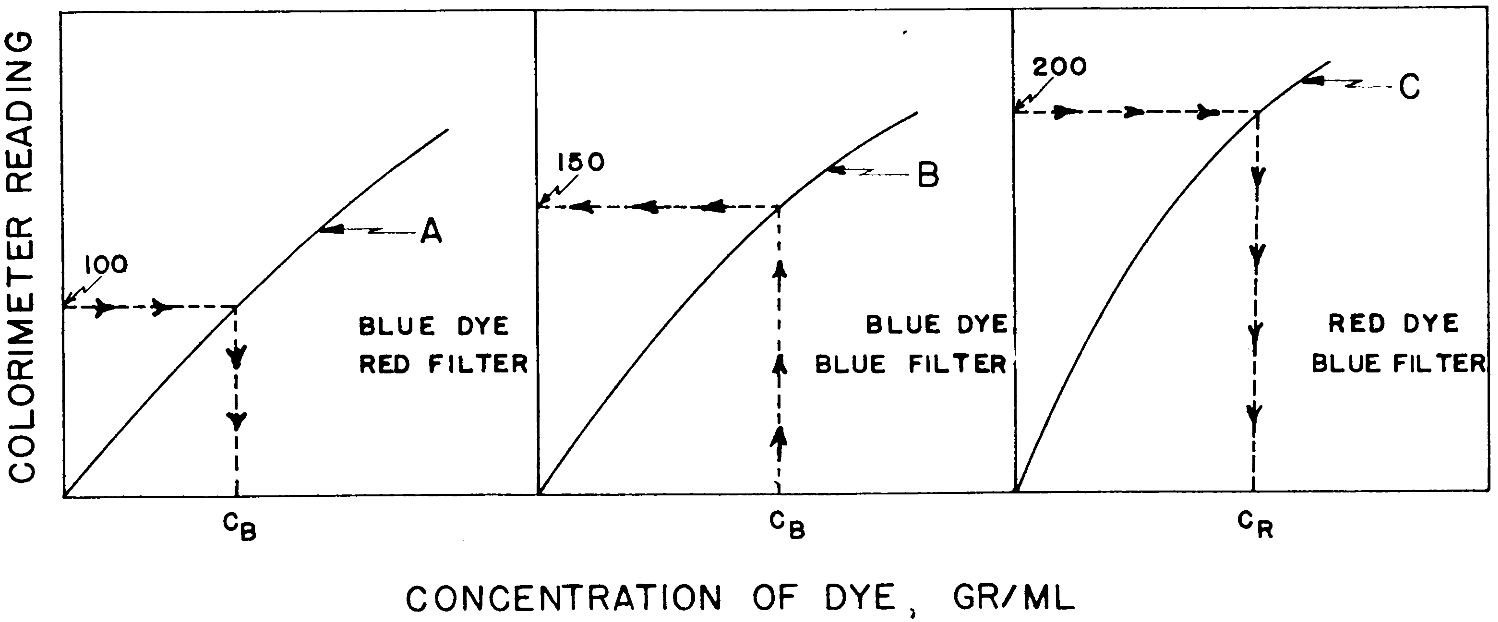


FIGURE 10. CALIBRATION CURVES FOR RED AND BLUE DYES WITH RED AND BLUE FILTERS (HYPOTHETICAL CASE).

This procedure was followed in analyzing various binary mixtures of red, yellow, and blue dyes (celanthrene red 3B, 2,6-dimethyldiaminoanthraquinone, and 1,4-diethyldiaminoanthraquinone, respectively). A similar procedure was followed in analyzing a mixture of the three dyes. In this case, however, in addition to the red and blue filters, a green filter and the appropriate calibration curves with the green filter were employed.

Data and Results

The data and results of this investigation are presented in this section in both tabular and graphical form.

Thermocouple Calibration. The calibration data for the feed and residue thermocouples for a temperature range between 60 and 225 degrees Centigrade is given in Table V, page 163, and the calibration curves are given in Figures 11 and 12, pages 164 and 165.

Colorimeter Calibration. Colorimeter readings for known concentrations of the various dyes employed in the investigation were made using the red, green, and blue filters to determine calibration curves. The data for the colorimeter calibration is given in Table VI, page 166, and shown graphically for the various dyes as follows:

Celanthrene Red 3B: Figures 13A and 13B, pages 167 and 168.

1,4-Diethyldiaminoanthraquinone: Figures 14A, 14B, and 14C, pages 169, 170, and 171.

2,6-Dimethyldiaminoanthraquinone: Figure 15, page 172.

1,4-Diisopropyldiaminoanthraquinone: Figure 16, page 173.

1,4-Dibutyldiaminoanthraquinone: Figure 17, page 174.

Constant Yield Oil. The data obtained from the molecular distillation of light and heavy mineral oils for use as a constant-yield oil is shown in Table VII, page 175. Table VIII, page 176, gives the data from the distillation of mixtures of both light and heavy mineral oils to indicate the extent to which a constant-yield oil could be prepared by merely mixing the two grades of mineral oil.

Colorimeter Corrections. The colorimeter readings of the various distillation fractions from the molecular distillation of the mixtures of light and heavy mineral oils are given in Table IX, page 177, for the blue, red, and green filters and the correction curves for these readings are shown in Figure 18, page 178. The proper correction was subtracted from the colorimeter readings during the analysis of the various fractions obtained during the distillations for dye concentration.

Continuous Temperature Rise Technique of Molecular Distillation. The data and results are given in Table X, page 179, for the molecular distillation of 1,4-diethyldiamineanthraquinone, 1,4-diisopropyldiaminoanthraquinone, and 1,4-dibutyldiaminoanthraquinone dyes using a continuous temperature rise during the collection of each fraction. The elimination curves for these distillations appear in Figure 19, page 180.

Discontinuous Temperature Rise Technique of Molecular Distillation. The data and results are given in Table XI, page 181, for the molecular distillation of celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone using a discontinuous temperature rise technique for the collection of each fraction. The elimination curves for these distillations appear in Figure 20, page 182.

Comparison of Continuous and Discontinuous Techniques. Figure 21, page 183, gives the elimination curves for 1,4-diethyldiaminoanthraquinone as obtained by the two techniques of operation, continuous and discontinuous temperature rise. The data for Figure 21 was obtained from Tables X and XI, pages 179 and 181, respectively.

Molecular Distillation of Single Anthraquinone Dyes. The data for the molecular distillation of the single anthraquinone dyes under conditions similar to those employed in the distillations of binary and tertiary mixtures are presented in Table XII, page 184.

Celanthrene Red 3B. The elimination curves for celanthrene red 3B are shown in Figure 22, page 185. Duplicate tests at 6 microns of mercury and a single test at 2 microns of mercury, absolute pressure, were made.

1,4-Diethyldiaminoanthraquinone. The elimination curve for 1,4-diethyldiaminoanthraquinone appears in Figure 23, page 186. One curve was drawn for duplicate distillations.

2,6-Dimethyldiaminoanthraquinone. Figure 24, page 187, presents the elimination curve from the distillation of 2,6-dimethyldiaminoanthraquinone.

Molecular Distillation of Binary Mixtures of Dyes. Various binary mixtures of celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone in a mineral constant-yield oil were molecularly distilled under the standardized conditions of operation.

Celanthrene Red 3B and 1,4-Diethyldiaminoanthraquinone. Binary mixtures of weight ratios of 2:1, 1:1, and 1:2-1/2 of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone were distilled. The data and results from the distillations appear in Table XIII, page 188, and the elimination curves of the single dyes from the mixture and the composite curves are shown in Figures 25, 26, and 27, pages 189, 190, and 191.

Celanthrene Red 3B and 2,6-Dimethyldiaminoanthraquinone. Table XIV, page 192, and Figure 28, page 193, present the data and results and elimination curves for the distillation of a binary mixture of equal weights of celanthrene red 3B and 2,6-dimethyldiaminoanthraquinone.

1,4-Diethyldiaminoanthraquinone and 2,6-Dimethyldiaminoanthraquinone. The data and results of the distillation of a binary mixture of equal weights of 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone are tabulated in Table XV, page 194. The elimination curves are given in Figure 29, page 195.

Separation of Binary Mixtures of Dyes. Data and results from attempts to separate binary mixtures of dyes by molecular redistillation are presented in tabular and graphical form as follows:

Extractive Redistillation. The cumulative fractions up to 140 degrees Centigrade obtained from the molecular distillation of a 2:1 weight ratio of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone were redistilled after the addition of heavy mineral oil to the oil solution of the dyes. The data and results of this "extractive" redistillation as well as the original distillation are given in Table XVI, page 196, and shown graphically in Figures 30A and 30B, pages 197 and 198.

Conventional Redistillation. Distillations were performed on two duplicate binary mixtures of equal weights of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone to obtain cumulative fractions up to 140 degrees Centigrade in sufficient volume for redistillation. Subsequent cumulative volumes obtained from the redistillation were again redistilled in an effort to study the separatory ability of the molecular still. The data for the initial distillations and the redistillations are given in Table XVII, page 199. The elimination and composite curves which were obtained appear in Figures 31A, 31B, and 31C, pages 200, 201, and 202.

Molecular Distillation of a Tertiary Mixture of Dyes. The data and results of the distillation of a tertiary mixture of equal weights of celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone are given in Table 18, page 203. Figure 32, page 204, presents the elimination and composite curves for the distillation.

TABLE V

Calibration Data for Feed and Residue Thermocouples

Temperature	Potentiometer Readings	
	Feed Thermocouple	Residue Thermocouple
°C	mv	mv
60	2.45	2.36
65	2.58	2.58
70	2.83	2.80
75	3.05	3.03
80	3.28	3.26
85	3.51	3.47
90	3.75	3.70
95	3.98	3.92
100	4.20	4.14
105	4.43	4.35
110	4.66	4.58
115	4.90	4.80
120	5.13	5.03
125	5.38	5.24
130	5.60	5.46
135	5.84	5.69
140	6.06	5.91
145	6.30	6.14
150	6.54	6.36
155	6.79	6.58
160	7.02	6.80
165	7.27	7.03
170	7.50	7.25
175	7.77	7.47
180	8.03	7.69
185	8.30	7.91
190	8.57	8.14
195	8.86	8.37
200	9.09	8.58
205	9.35	8.80
210	9.62	9.02
215	9.88	9.26
220	10.15	9.48
225	10.40	9.70

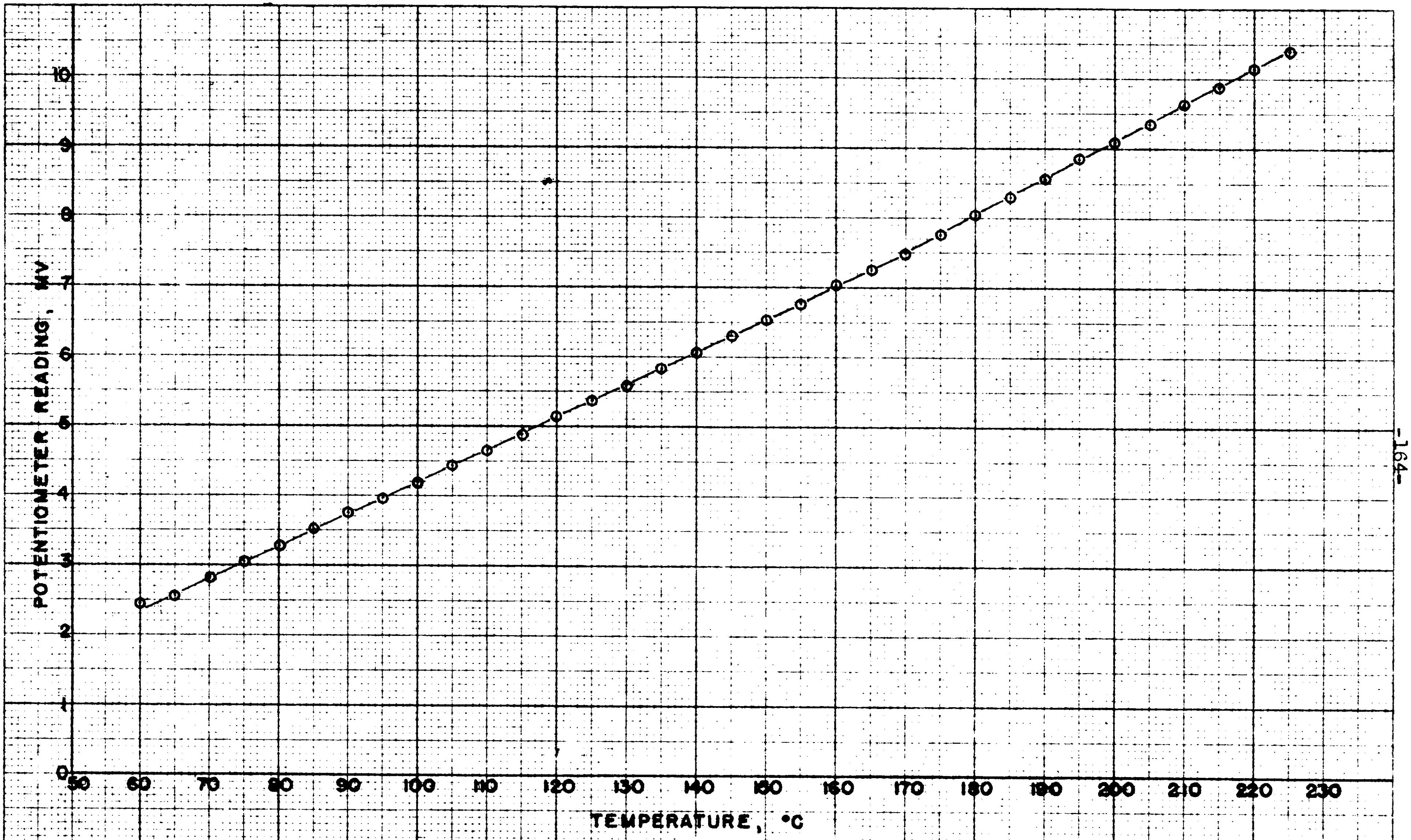


FIGURE 11. CALIBRATION CURVE FOR FEED THERMOCOUPLE

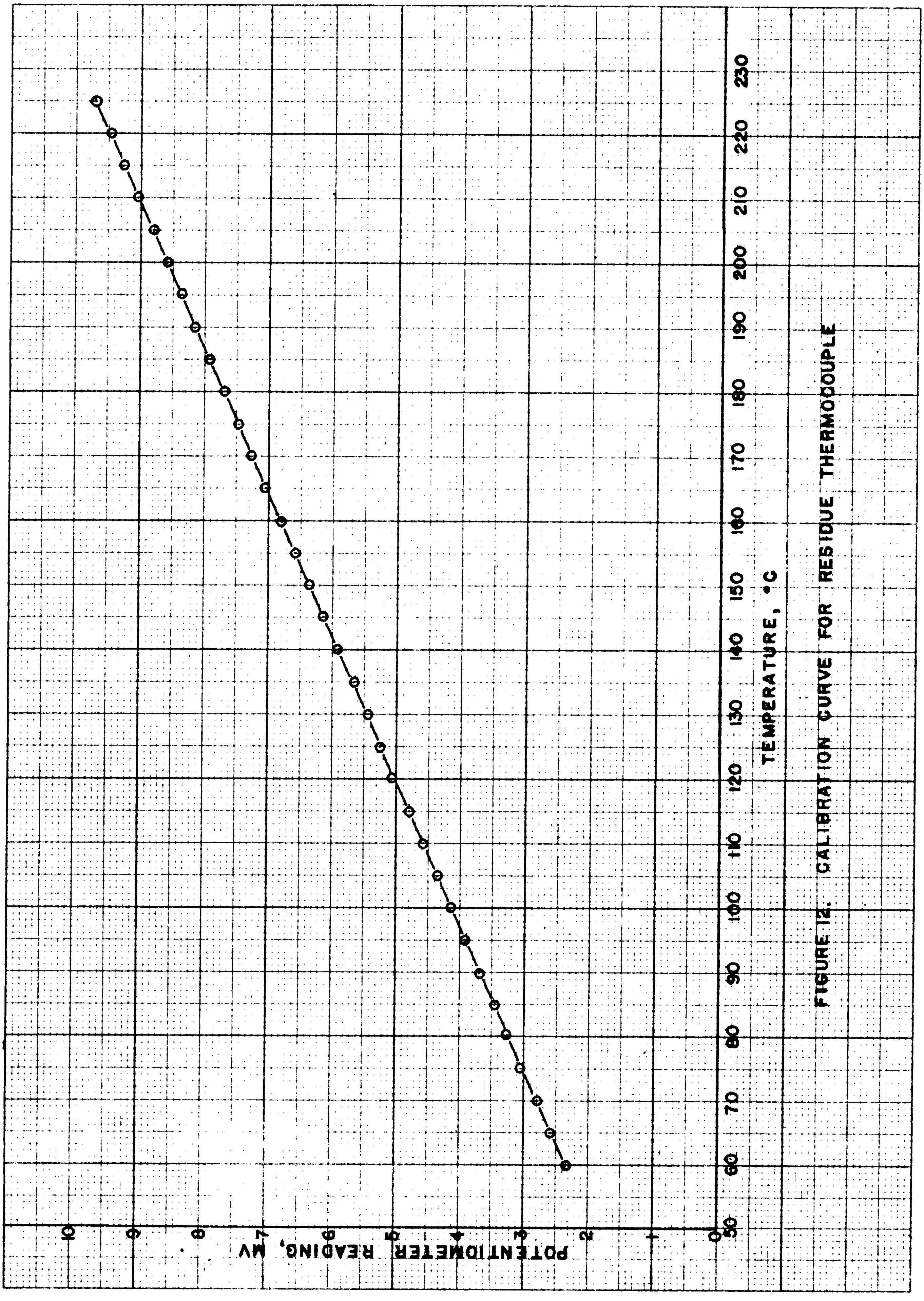


FIGURE 12. CALIBRATION CURVE FOR RESIDUE THERMOCOUPLE

TABLE VI

Calibration Data for Colorimeter Using Various Oil-Dye Mixtures

Dye	Concentration of Dye[a] gm/100 ml	Colorimeter Readings		
		Blue Filter	Red Filter	Green Filter
Celanthrene Red 3B				
Test 1	0.0142	176		830
	0.0071	92		438
	0.0036	49		222
	0.0018	27		115
	0.0009	15		59
Test 2	0.0142	177		835
	0.0071	94		439
	0.0036	50		222
	0.0018	27		115
	0.0009	15		59
1,4-Diethyldiaminoanthraquinone				
Test 1	0.0202	155	239	975
	0.0101	85	197	625
	0.0050	45	159	357
	0.0025	23	111	192
	0.0013	12	73	111
	0.0006	7	43	52
Test 2	0.0291	207	258	---
	0.0145	116	219	775
	0.0073	62	169	455
	0.0036	33	134	258
	0.0018	19	92	138
	0.0009	10	54	73
2,6-Dimethyldiaminoanthraquinone				
Test 1	0.0020	189		
	0.0010	110		
	0.0005	63		
	0.0002	34		
	0.0001	19		
Test 2	0.0019	195		
	0.0010	114		
	0.0005	65		
	0.0002	36		
	0.0001	18		
1,4-Diisopropyldiaminoanthraquinone	0.0491	329		
	0.0245	196		
	0.0164	150		
	0.0123	113		
	0.0082	83		
	0.0041	41		
1,4-Dibutyldiaminoanthraquinone	0.0600	350		
	0.0250	200		
	0.0125	112		
	0.0063	60		
	0.0032	30		

[a] All samples employed light mineral oil as dye solvent.

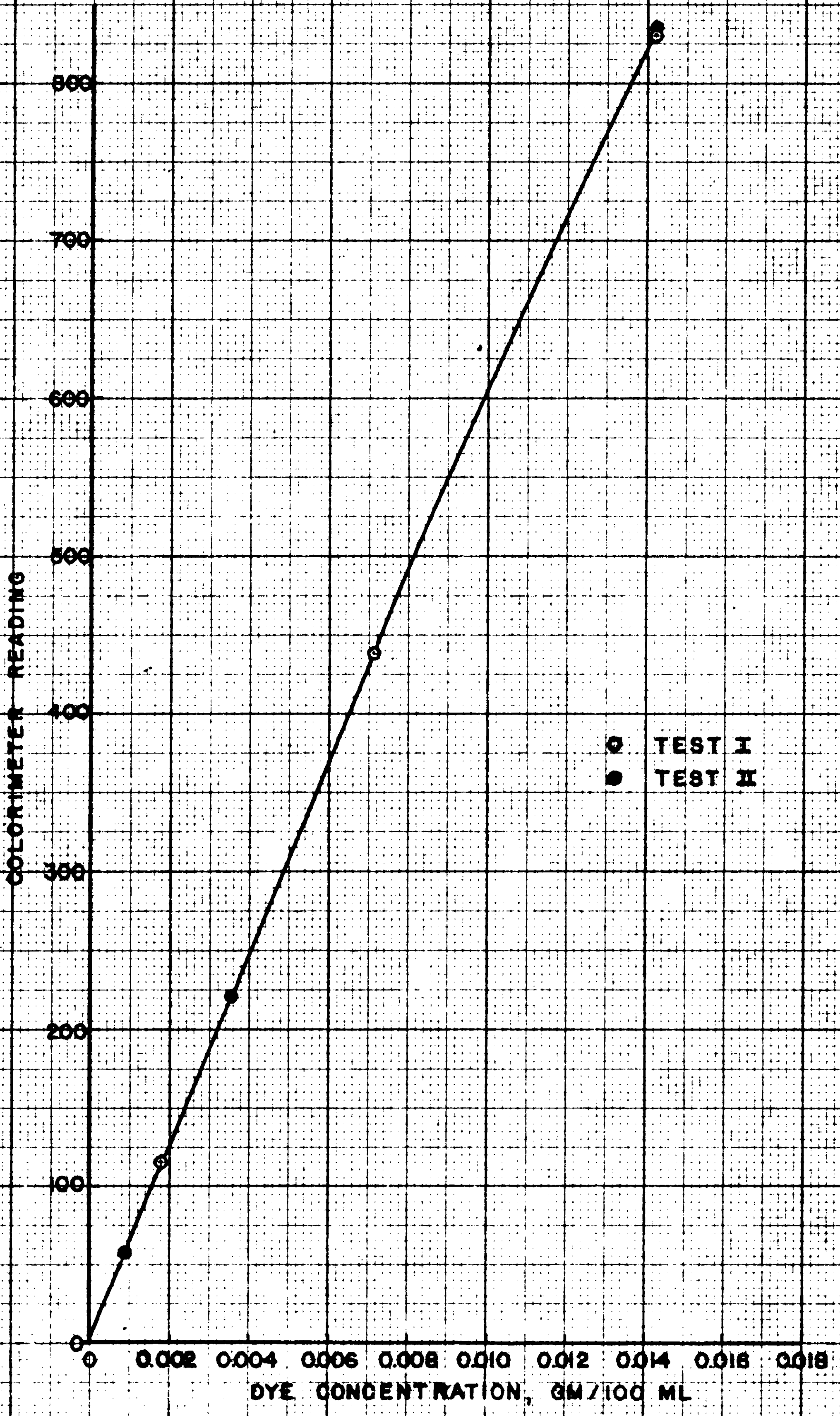


FIGURE 13A. COLORIMETRIC CALIBRATION CURVE FOR CELANTHRENE RED 3B DYE, USING THE GREEN FILTER.

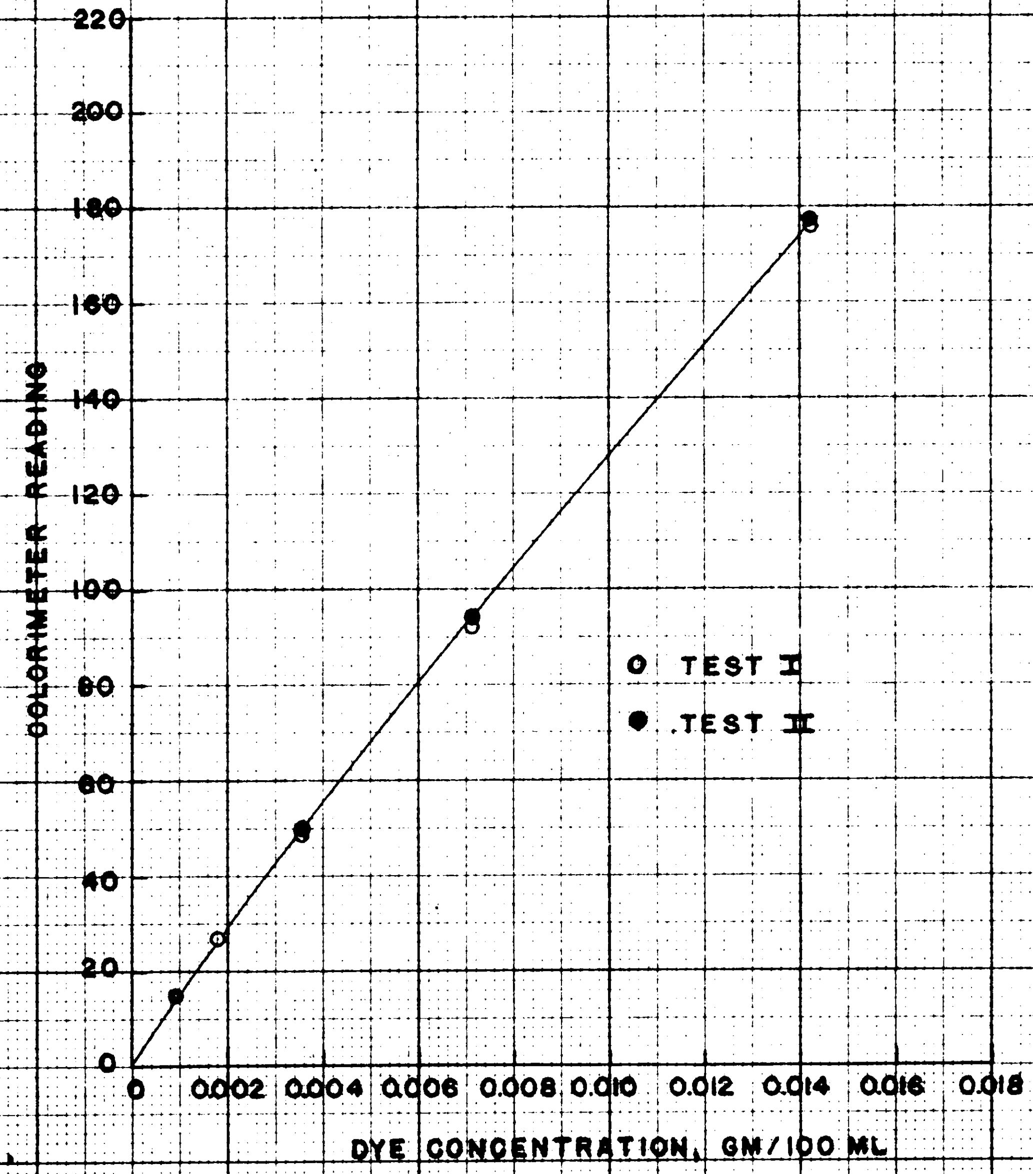


FIGURE 13B. COLORIMETRIC CALIBRATION CURVE FOR CELANTHRENE RED 3B DYE USING THE BLUE FILTER.

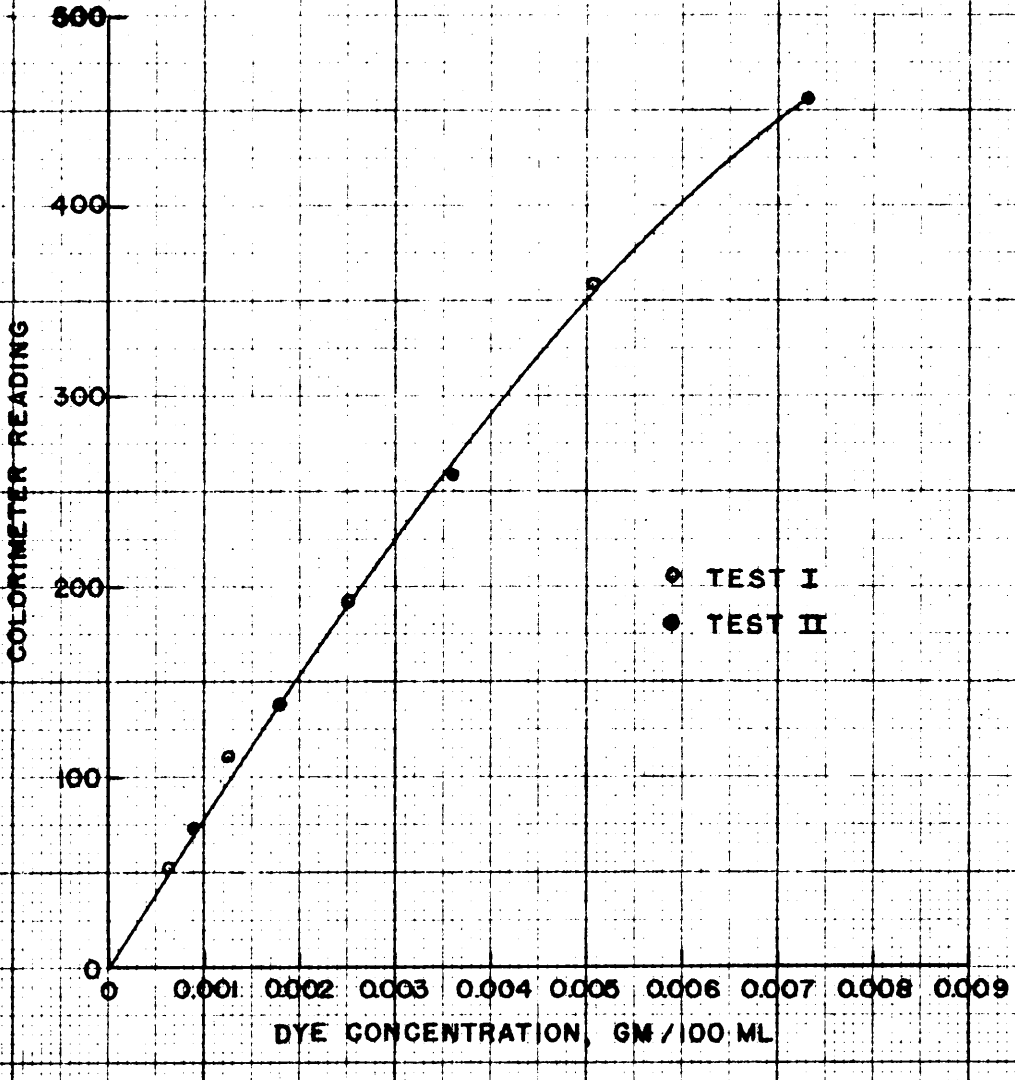


FIGURE 14A. COLORIMETRIC CALIBRATION CURVE FOR
1,4 - DIETHYLDIAMINOANTHRAQUINONE DYE
USING THE GREEN FILTER

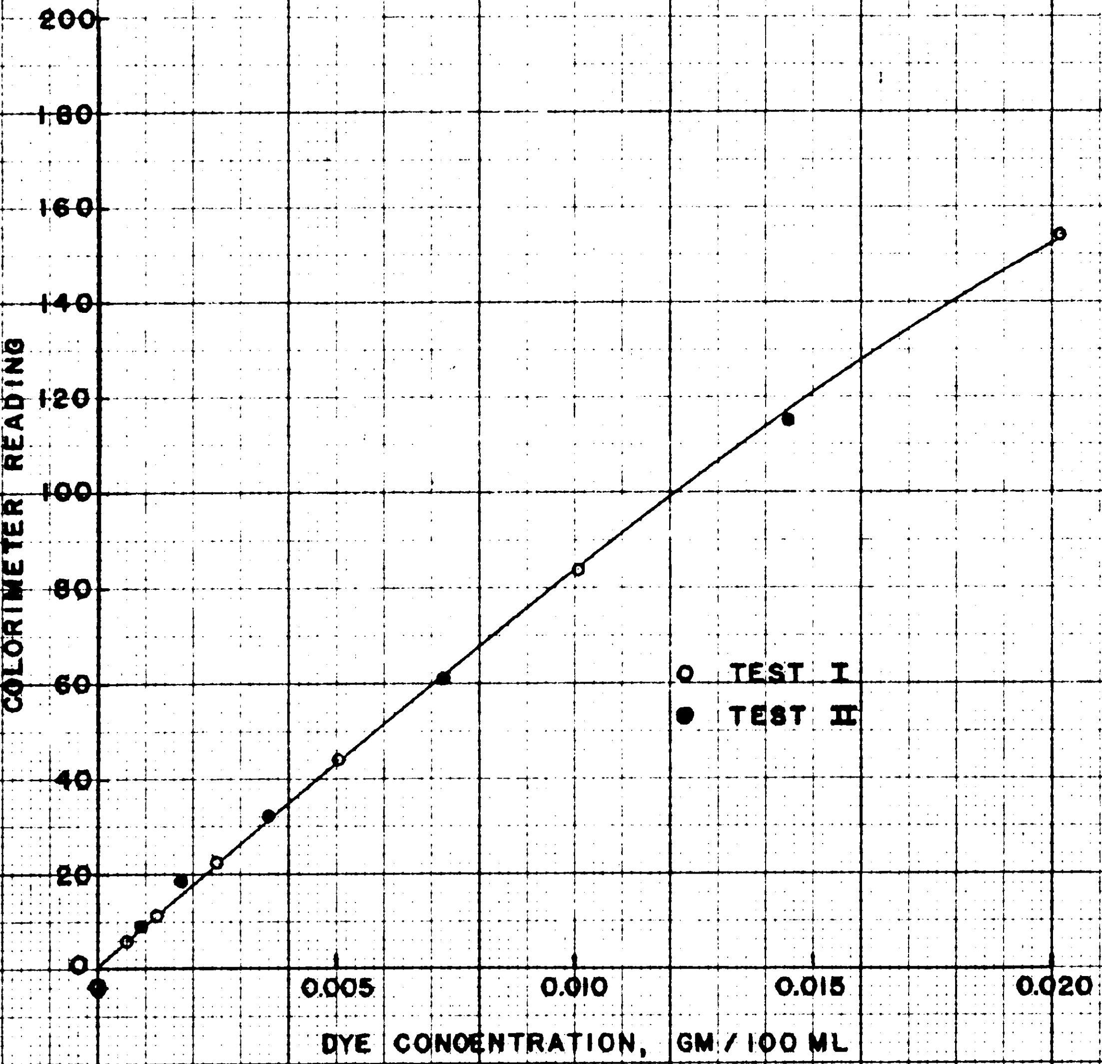


FIGURE 14B COLORIMETRIC CALIBRATION CURVE FOR 1,4-DIETHYLDIAMINOANTHRAQUINONE DYE USING THE BLUE FILTER

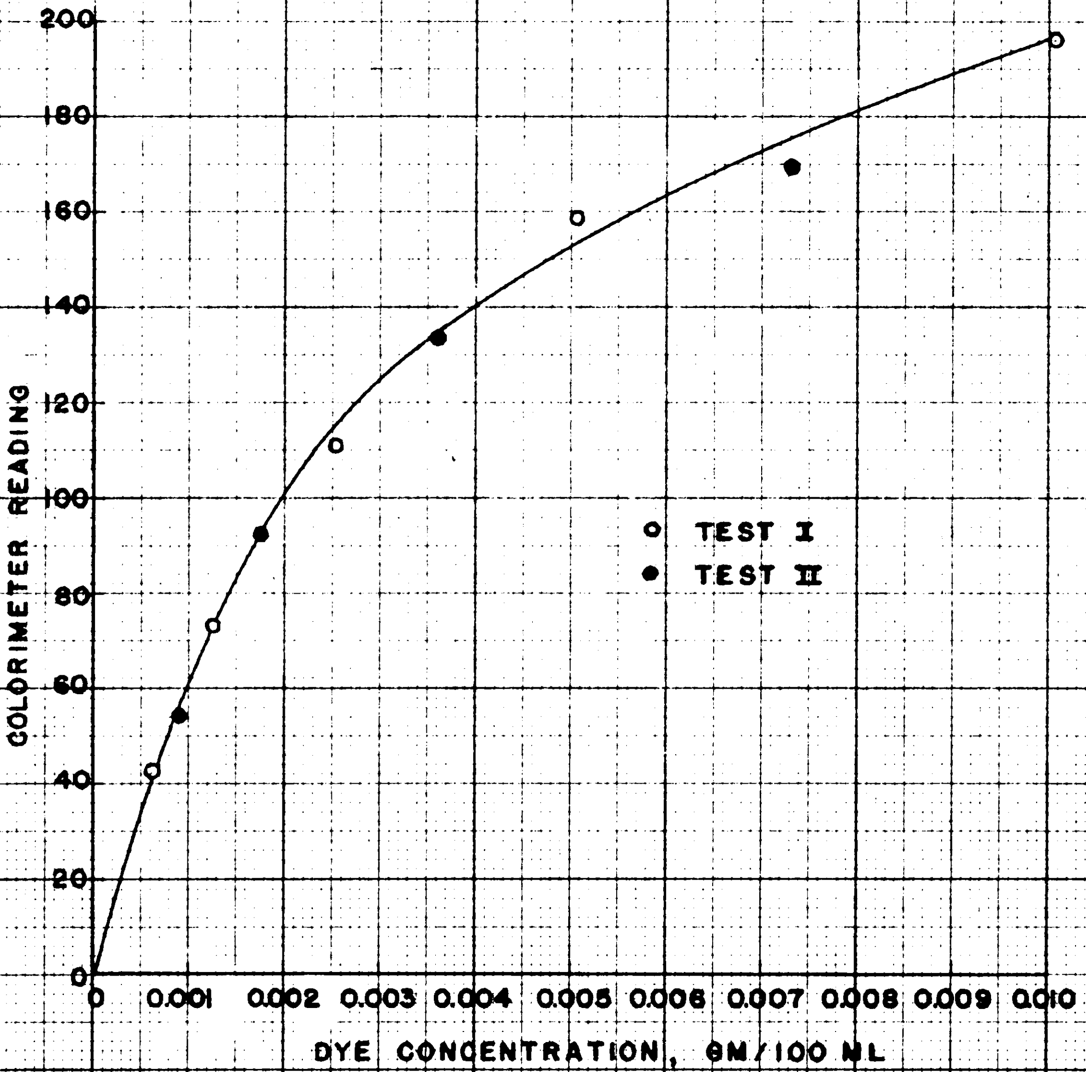


FIGURE 14C. COLORIMETRIC CALIBRATION CURVE
FOR 1,4-DIETHYLDIAMINOANTHRAQUINONE
DYE USING THE RED FILTER.

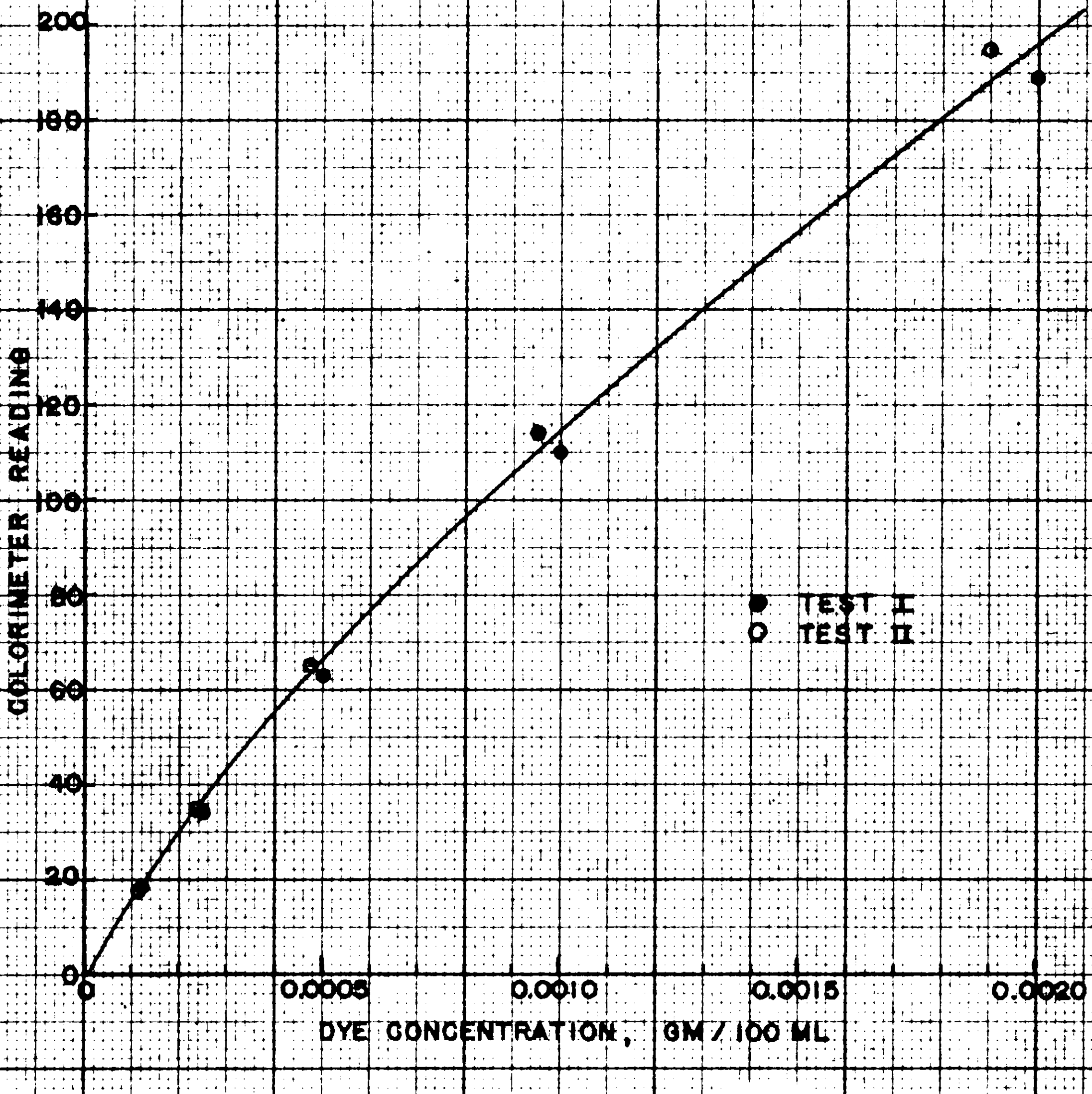


FIGURE 15. COLORIMETRIC CALIBRATION CURVE FOR 2,6-DIMETHYLDIAMINOANTHRAQUINONE DYE USING THE BLUE FILTER.

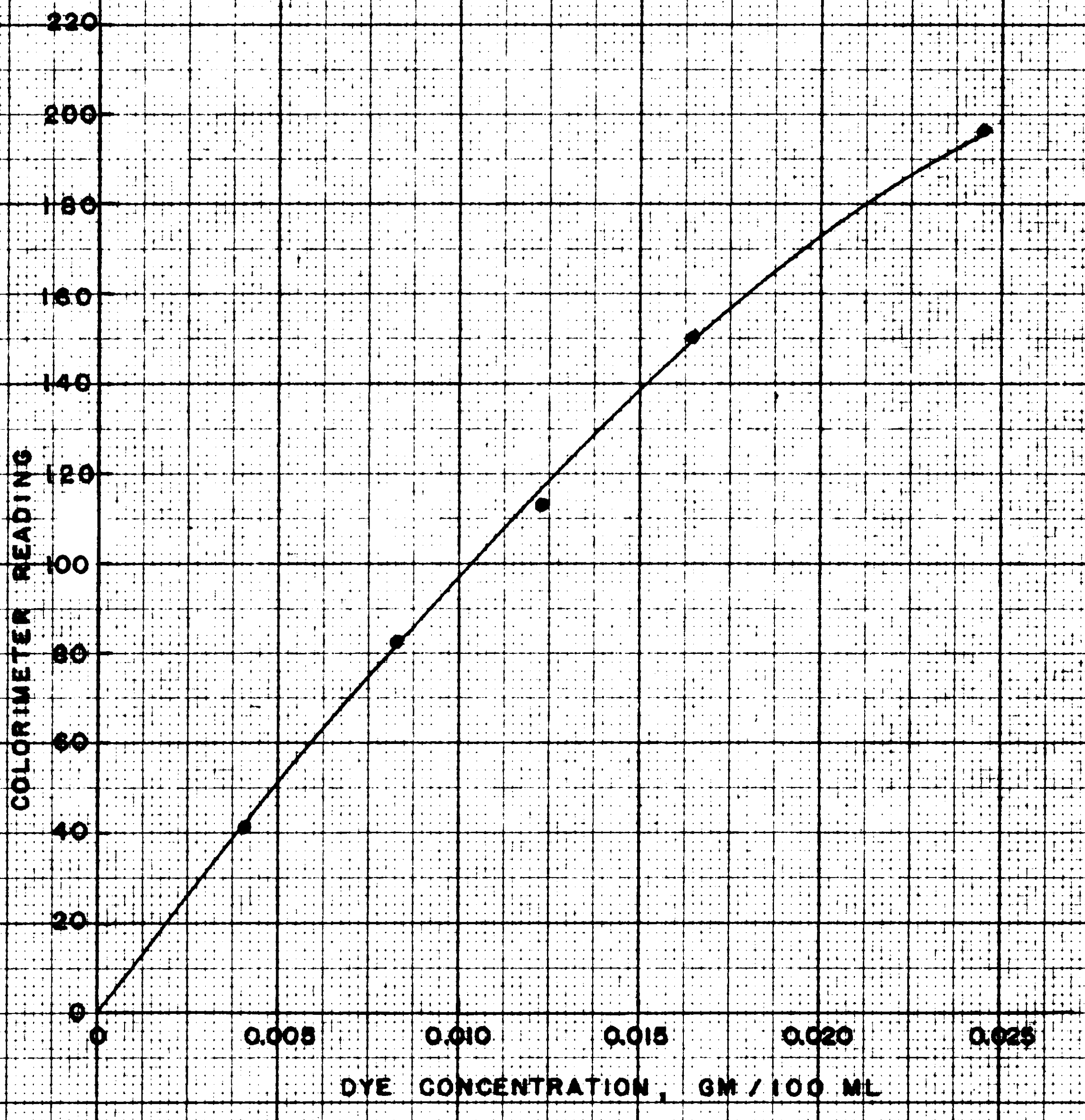


FIGURE 16. COLORIMETRIC CALIBRATION CURVE FOR 1,4- DIISOPROPYLDIAMINOANTHRAQUINONE DYE USING THE BLUE FILTER.

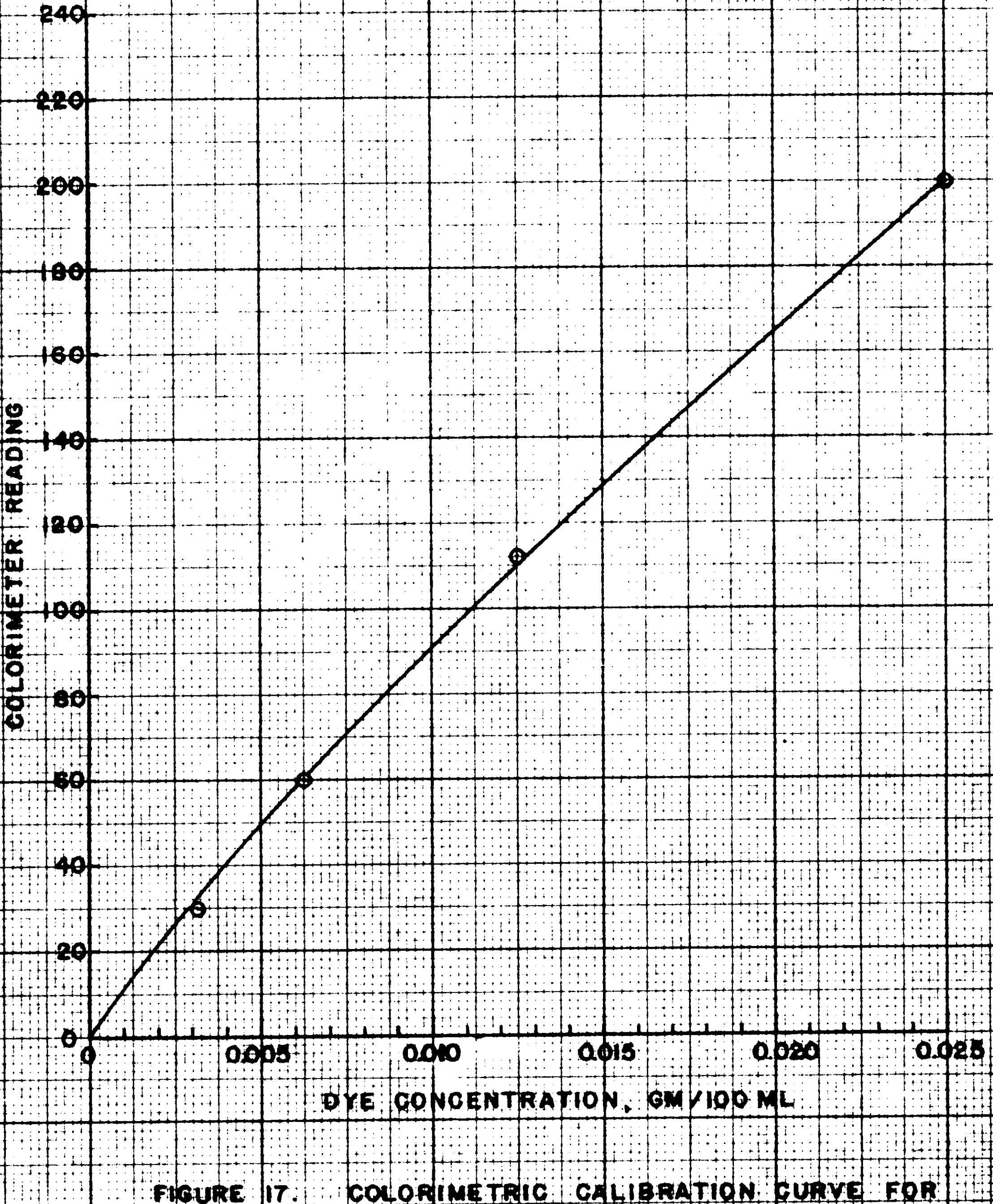


FIGURE 17. COLORIMETRIC CALIBRATION CURVE FOR 1,4 - DIBUTYLDIAMINOANTHRAQUINONE DYE USING THE BLUE FILTER.

TABLE VII

Typical Molecular Distillation of Light and Heavy Mineral Oils for the Preparation of a Constant-Yield Oil

Feed Rate: 122 ± 3 ml/min
Rotor Speed: 1720 ± 5 rpm
Pressure: 2 ± 1 microns
Feed-Residue ΔT: 10 °C
Fractions Collected Continuously During Temperature Rise

Type of Oil	Temperature of Fraction	Collection Time		Volume of Fraction		Yield of Fraction [a]	
		Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
	°C	min	min	ml	ml	vol %	vol %
Light Mineral Oil	90 - 100	55	65	112	118	16.0	16.6
	100 - 110	60	60	178	168	25.4	23.6
	110 - 120	60	55	208	190	29.6	26.7
	120 - 130	65	55	115	105	16.4	14.8
	Above 130	--	--	89	130	12.6	18.3
Heavy Mineral Oil	100 - 110	40	55	10	10	1.4	1.4
	110 - 120	55	35	46	30	6.5	4.3
	120 - 130	45	45	62	60	8.7	8.6
	130 - 140	45	50	80	96	11.3	13.7
	140 - 150	45	45	96	103	13.5	14.7
	150 - 160	40	60	105	121	14.7	17.2
	160 - 170	30	50	90	100	12.7	14.3
	170 - 180	35	30	113	95	15.9	13.6
	Above 180	--	--	109	86	15.3	12.2

[a] Yield of fraction is the volume per cent of the original feed.

TABLE VIII

Distillation of Light and Heavy Mineral Oil Mixtures for Preparation of Constant-Yield Oil

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 1720 ± 5 rpm
Pressure: 2 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 2

Temperature of Fraction	Volume of Fraction		Yield of Fraction	
	Test 1	Test 2	Test 1	Test 2
°C	ml	ml	vol %	vol %
100	34	30	4.5	4.2
110	71	72	9.5	10.0
120	92	90	12.3	12.5
130	92	84	12.3	11.7
140	88	92	11.7	12.8
150	79	76	10.5	10.5
160	73	67	9.7	9.3
170	82	63	10.9	8.7
180	26	33	3.5	4.6
Above 180	113	113	15.1	15.7
Total	750	720	100.0	100.0

TABLE IX

Colorimeter Analysis of Constant-Yield Oil Fractions Using Light Mineral Oil as Standard

Temperature of Fraction °C	Colorimeter Reading [a] Blue Filter[b]	Red Filter[b]	Green Filter[b]
90	2	2	2
100	2	2	2
110	3	3	3
120	3	3	3
130	4	3	4
140	8	6	6
150	9	6	6
160	12	6	6
170	15	8	9
180	18	9	12
190	20	10	14

[a] **Colorimeter reading as referred to zero reading for Light Mineral Oil standard.**

[b] Approximate Spectral Range of Filters:

Blue 400 - 465 millimicrons
Green 500 - 570 millimicrons
Red 640 - 700 millimicrons

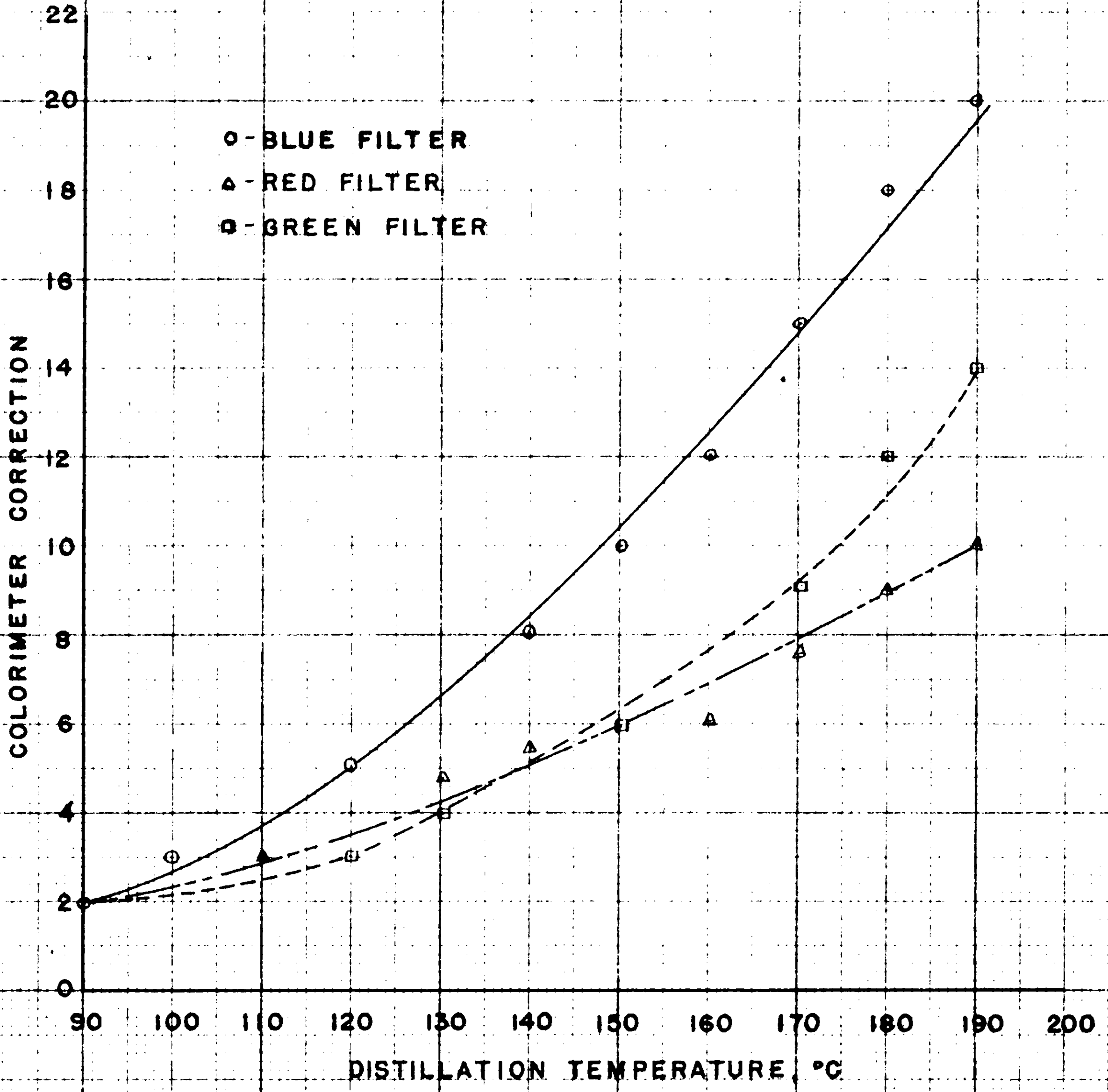


FIGURE 18. COLORIMETER CORRECTIONS FOR THE VARIOUS FILTERS FOR THE TEMPERATURE FRACTIONS OBTAINED FROM THE MOLECULAR DISTILLATION OF A MINERAL OIL BLANK.

TABLE X

Data and Results for the Molecular Distillation of 1,4-Diethyldiamineanthraquinone, 1,4-Diisopropyldiamineanthraquinone, and 1,4-Dibutyldiamineanthraquinone Dyes Using the Continuous Temperature Rise Technique of Collecting Distillate Fractions

Feed Rate: 122 ± 3 ml/min
Rotor Speed: 1720 ± 5 rpm
Pressure: 2 ± 1 microns
Feed-Residue ΔT: 10 °C
Fractions Collected During Continuous Temperature Rise

Dye	Temperature of Fraction °C	Collection Time min	Volume ml	Concentration of Dye gm/100 ml	Weight of Dye gm	Yield of Dye wt %	Elimination Maximum °C
1,4-Diethyldiamine-anthraquinone	80 - 90	125	25	0.0020	0.00052	1.1	131
	90 - 100	90	62	0.0028	0.00172	3.6	
	100 - 110	45	48	0.0070	0.00336	7.0	
	110 - 120	40	43	0.0162	0.00695	14.5	
	120 - 130	45	62	0.0288	0.01786	37.1	
	130 - 140	40	38	0.0256	0.00973	20.2	
	140 - 150	35	33	0.0112	0.00370	7.7	
	150 - 160	40	25	0.0058	0.00145	3.0	
1,4-Diisopropyl-diamine-anthraquinone	80 - 90	110	22	0.0030	0.00066	1.2	141
	90 - 100	75	56	0.0032	0.00179	3.2	
	100 - 110	55	72	0.0046	0.00331	5.9	
	110 - 120	60	71	0.0079	0.00561	10.0	
	120 - 130	50	66	0.0134	0.00884	15.7	
	130 - 140	45	68	0.0192	0.01306	23.3	
	140 - 150	40	60	0.0154	0.00924	16.4	
	150 - 160	30	64	0.0090	0.00576	10.3	
	160 - 170	45	86	0.0044	0.00378	6.7	
1,4-Dibutyldiamine-anthraquinone	80 - 90	100	13	0.0021	0.00042	0.8	152
	90 - 100	78	57	0.0022	0.00121	2.4	
	100 - 110	52	72	0.0019	0.00137	2.7	
	110 - 120	60	91	0.0019	0.00173	3.4	
	120 - 130	60	105	0.0025	0.00263	5.2	
	130 - 140	50	87	0.0051	0.00444	8.8	
	140 - 150	55	78	0.0114	0.00889	17.6	
	150 - 160	45	45	0.0184	0.00828	16.4	
	160 - 170	40	46	0.0176	0.00810	16.0	
	170 - 180	30	45	0.0140	0.00630	12.5	

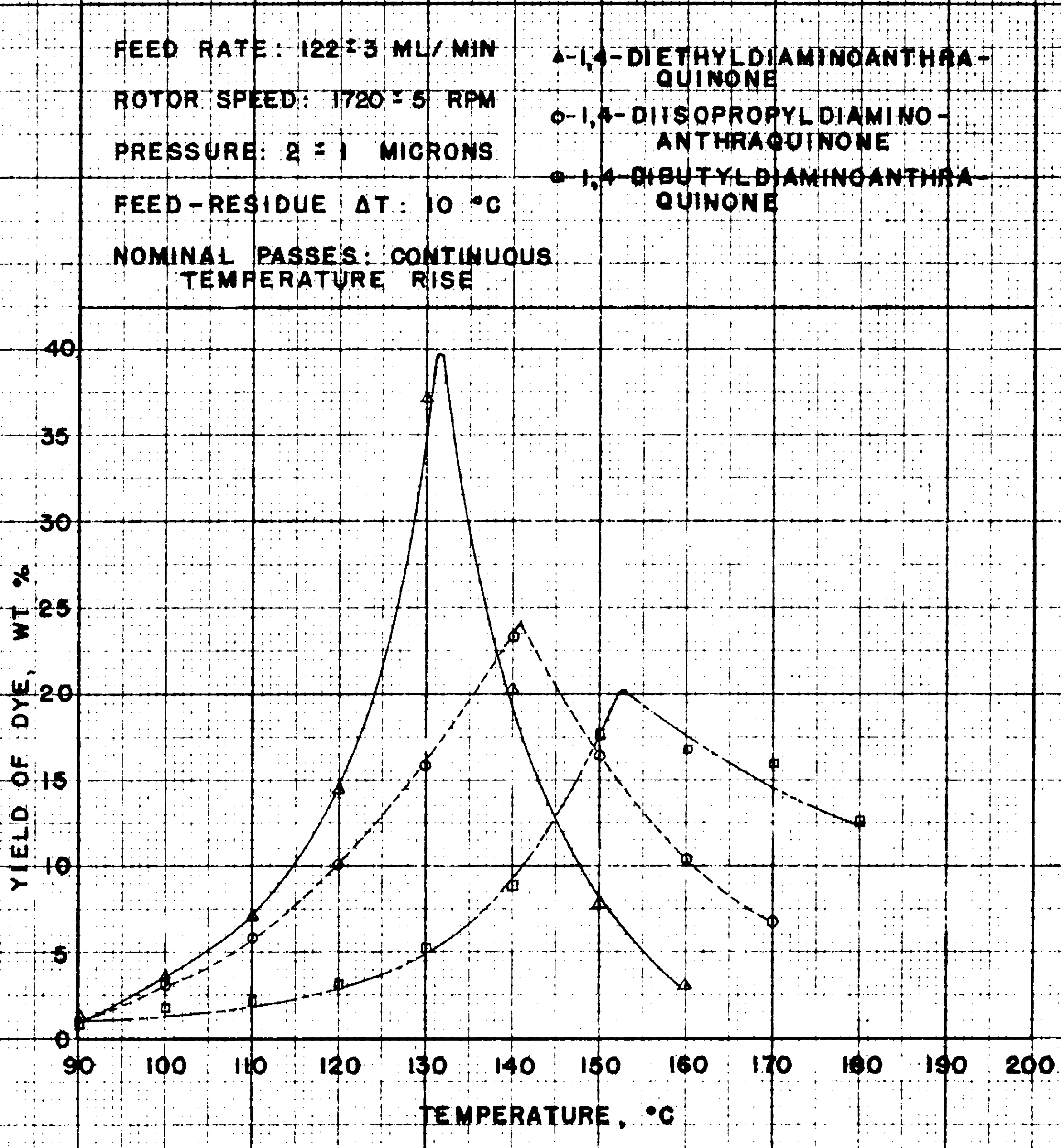


FIGURE 19. ELIMINATION CURVES FOR MOLECULAR DISTILLATION OF VARIOUS DYES EMPLOYING THE CONTINUOUS TEMPERATURE RISE TECHNIQUE.

TABLE XI

Data and Results for the Molecular Distillation of 1,4-Diethyldiamineanthraquinone, Celanthrene Red 3B, and 2,6-Dimethyldiamineanthraquinone Dyes Using the Discontinuous Temperature Rise Technique of Collecting Distillate Fractions

Feed Rate: 122 ± 3 ml/min
Rotor Speed: 1720 ± 5 rpm
Pressure: 2 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 5

Dye	Temperature of Fraction °C	Volume ml	Concentration of Dye gm/100 ml	Weight of Dye gm	Yield of Dye wt %	Elimination Maximum °C
Celanthrene Red 3B	100	31	0.0068	0.00209	9.9	115
	110	66	0.0082	0.00538	25.4	
	120	93	0.0067	0.00618	29.1	
	130	96	0.0036	0.00346	16.4	
	140	85	0.0014	0.00115	5.4	
1,4-Diethyldiamine-anthraquinone	90	12	0.0038	0.00046	1.4	151
	100	39	0.0017	0.00066	2.0	
	110	69	0.0012	0.00083	2.5	
	120	80	0.0029	0.00232	6.9	
	130	82	0.0038	0.00312	9.3	
	140	86	0.0057	0.00491	14.6	
	150	81	0.0087	0.00705	21.0	
	160	65	0.0084	0.00546	16.3	
	170	62	0.0057	0.00354	10.7	
2,6-Dimethyldiamine-anthraquinone	100	45	0.00017	0.00008	1.3	154
	110	57	0.00020	0.00011	2.0	
	120	98	0.00028	0.00027	4.7	
	130	90	0.00050	0.00045	7.8	
	140	88	0.00100	0.00088	15.2	
	150	78	0.00185	0.00144	24.9	
	160	60	0.00240	0.00144	24.9	
	170	53	0.00153	0.00081	14.0	

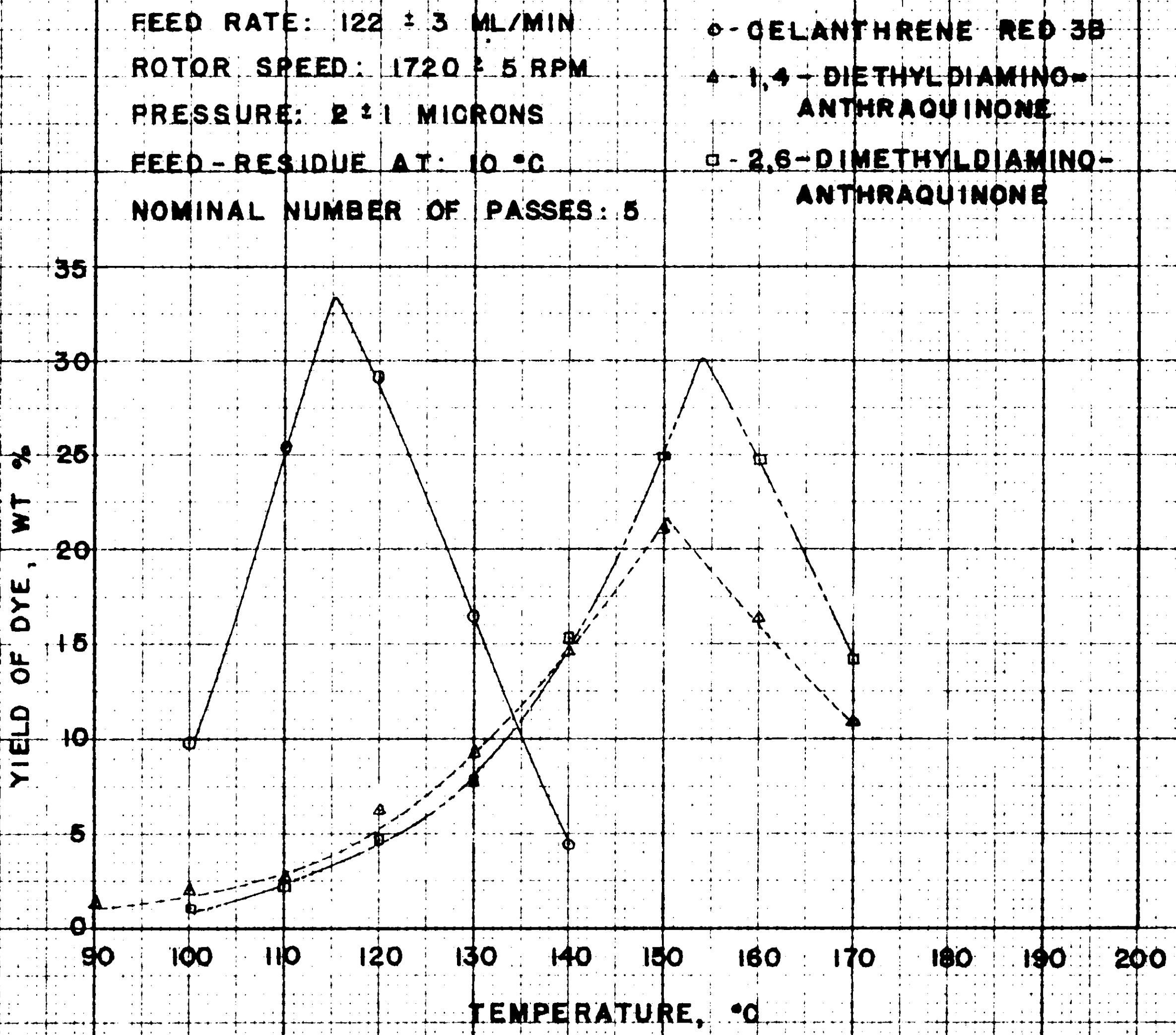


FIGURE 20. ELIMINATION CURVES FOR THE MOLECULAR DISTILLATION OF VARIOUS DYES EMPLOYING THE DISCONTINUOUS TEMPERATURE RISE TECHNIQUE.

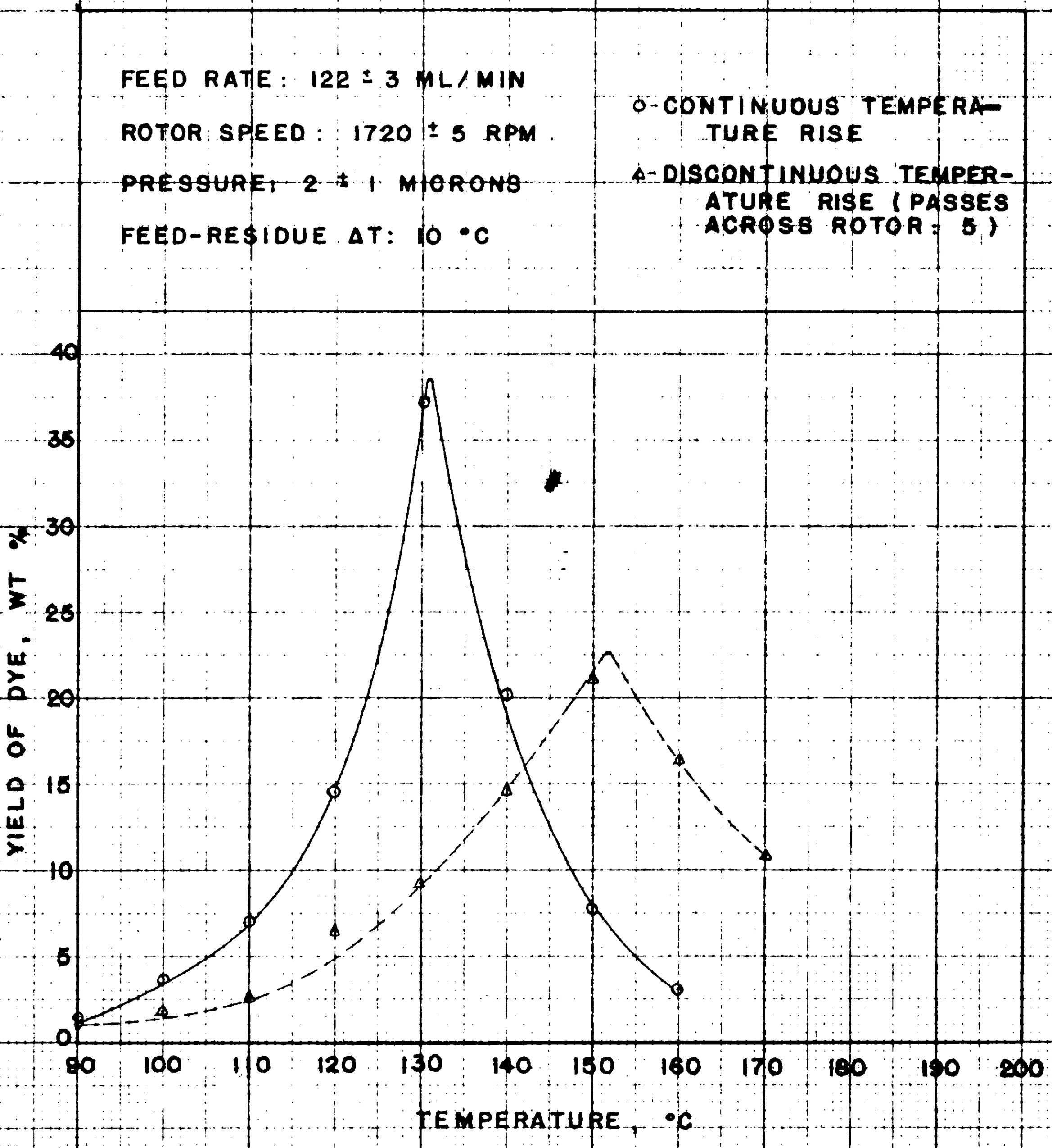


FIGURE 21. ELIMINATION CURVES FOR THE MOLECULAR DISTILLATION OF 1,4-DIETHYLDIAMINOANTHRAQUINONE EMPLOYING BOTH THE CONTINUOUS AND DISCONTINUOUS TEMPERATURE RISE TECHNIQUES.

TABLE XII

Data and Results for the Molecular Distillation of Various Anthraquinone Dyes

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 2000 ± 50 rpm
Nominal Number of Passes: 2
Feed-Residue ΔT: 10 °C

Dye	Pressure	Temperature of Fraction	Volume	Concentration of Dye	Weight of Dye	Yield of Dye	Elimination Maximum
	microns	°C	ml	gm/100 ml	gm	wt %	°C
Celanthrene Red 3B	2	100	33	0.00450	0.00149	11.5	113
		110	75	0.00450	0.00338	26.1	
		120	78	0.00390	0.00304	23.5	
		130	90	0.00230	0.00207	16.0	
		140	89	0.00110	0.00098	7.5	
		150	93	0.00065	0.00061	4.7	
Celanthrene Red 3B	6	100	20	0.00280	0.00056	4.3	121
		110	54	0.00360	0.00195	16.6	
		120	85	0.00370	0.00316	26.8	
		130	100	0.00221	0.00221	18.8	
		140	98	0.00090	0.00089	7.6	
		150	82	0.00023	0.00017	1.4	
		160	59	0.00004	0.00002	0.2	
Celanthrene Red 3B	6	100	19	0.00289	0.00055	4.4	121
		110	51	0.00375	0.00193	16.4	
		120	83	0.00390	0.00324	27.4	
		130	92	0.00270	0.00248	20.0	
		140	91	0.00122	0.00111	9.4	
		150	81	0.00024	0.00019	1.6	
		160	72	0.00013	0.00009	0.8	
1,4-Diethyldiamino-anthraquinone	6	110	46	0.00061	0.00028	1.9	152
		120	69	0.00095	0.00066	4.5	
		130	81	0.00164	0.00133	9.0	
		140	81	0.00295	0.00239	16.2	
		150	82	0.00443	0.00363	24.6	
		160	57	0.00490	0.00280	19.0	
		170	52	0.00408	0.00212	14.4	
		180	38	0.00278	0.00106	7.1	
1,4-Diethyldiamino-anthraquinone	6	110	51	0.00037	0.00019	1.6	152
		120	83	0.00061	0.00055	4.6	
		130	92	0.00136	0.00125	10.6	
		140	91	0.00247	0.00225	19.0	
		150	81	0.00340	0.00275	23.4	
		160	72	0.00336	0.00241	20.6	
		170	46	0.00251	0.00115	9.8	
		180	38	0.00145	0.00055	4.8	
2,6-Dimethyldiamino-anthraquinone	6	110	39	0.00018	0.00007	0.9	159
		120	73	0.00032	0.00023	3.2	
		130	82	0.00061	0.00050	7.0	
		140	71	0.00118	0.00084	10.7	
		150	82	0.00192	0.00157	21.8	
		160	72	0.00258	0.00185	25.8	
		170	59	0.00254	0.00150	20.9	
		180	31	0.00200	0.00062	8.6	

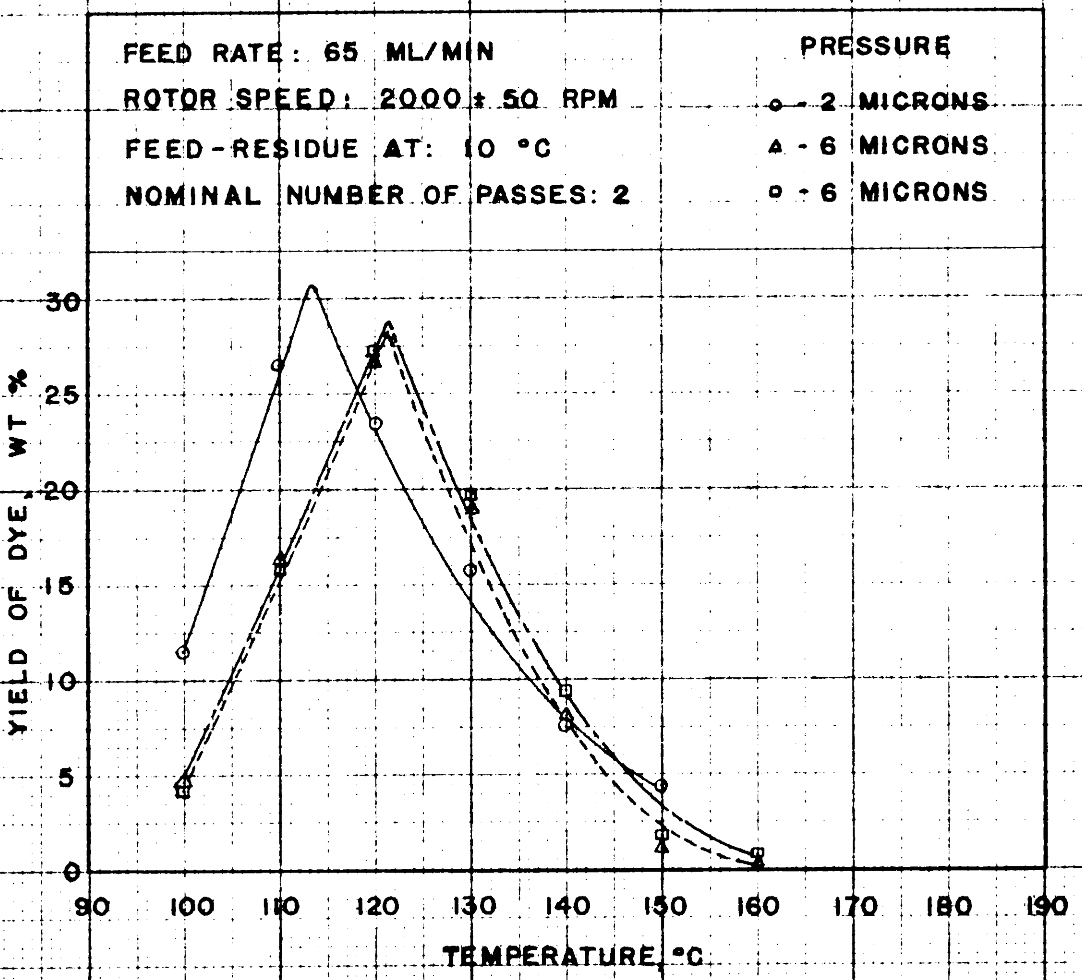


FIGURE 22. ELIMINATION CURVES FOR THE MOLECULAR DISTILLATION OF CELANTHRENE RED 3B.

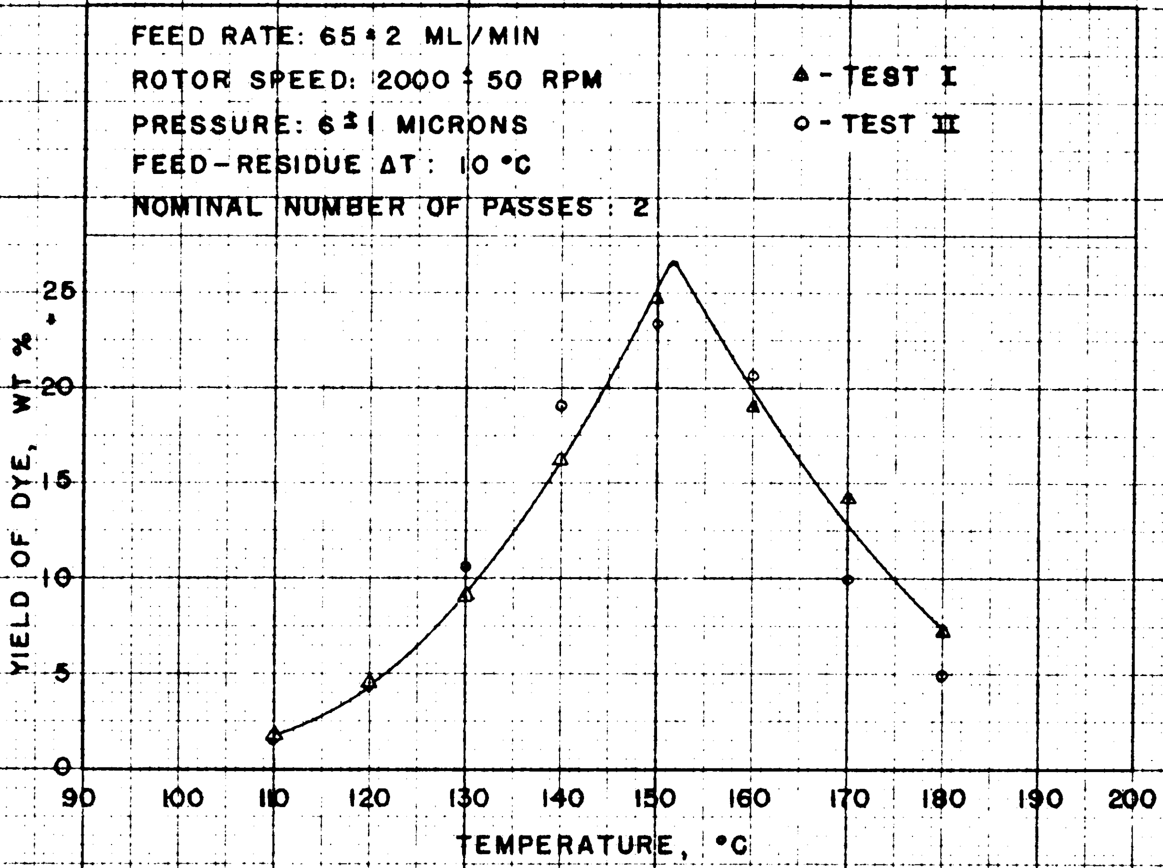


FIGURE 23. ELIMINATION CURVES FOR THE MOLECULAR DISTILLATION OF 1,4-DIETHYLDIAMINOANTHRAQUINONE.

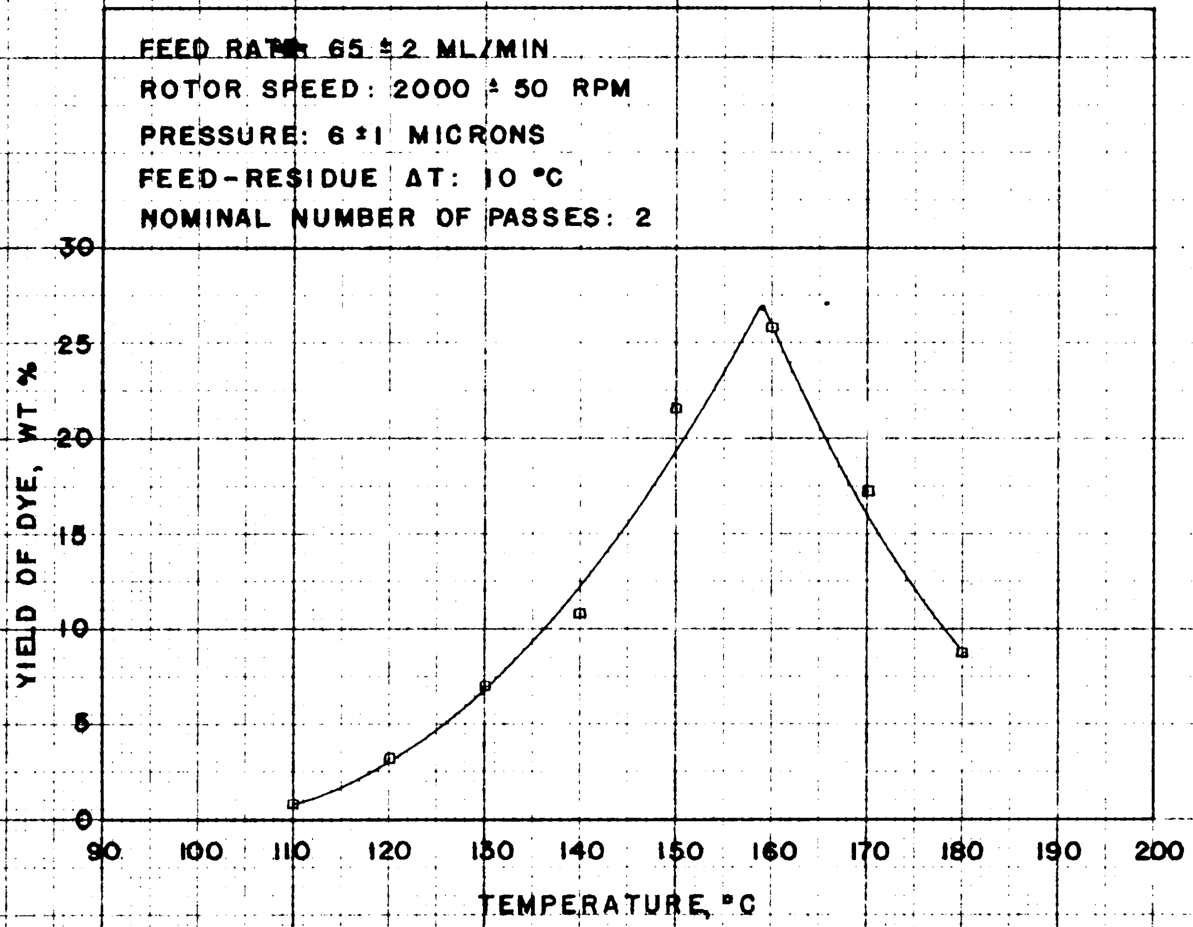


FIGURE 24. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF 2,6-DIMETHYLDIAMINOANTHRAQUINONE.

TABLE XIII

Data and Results for the Molecular Distillation of Various Binary Mixtures of Celanthrene Red 3B and 1,4-Diethyldiamineanthraquinone Dyes

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 2000 ± 50 rpm
Pressure: 6 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 2

Dye Ratio CR:DE	Temperature of Fraction	Volume	Concentration of Dye		Weight of Dye		Yield of Dye		
			CR [a]	DE [a]	CR	DE	CR	DE	Composite
wt:wt	°C	ml	gm/100 ml	gm/100 ml	gm	gm	wt %	wt %	wt %
2:1	100	26	0.00550	0.00035	0.00110	0.00009	3.7	0.3	4.0
	110	50	0.00648	0.00040	0.00325	0.00020	10.8	0.7	11.5
0.0200 gm	120	71	0.00620	0.00061	0.00441	0.00043	14.7	1.4	16.1
CR	130	73	0.00468	0.00113	0.00342	0.00083	11.7	2.8	14.2
0.0100 gm	140	66	0.00305	0.00180	0.00202	0.00143	6.7	4.8	11.5
DE	150	80	0.00120	0.00308	0.00096	0.00246	3.2	8.2	11.4
	160	57	0.00130	0.00335	0.00074	0.00191	2.5	6.3	8.8
	170	54	0.00130	0.00295	0.00070	0.00159	2.3	5.3	7.6
	180	40	0.00135	0.00190	0.00054	0.00076	1.8	2.5	4.3
1:1	100	19	0.00289	0.00023	0.00055	0.00004	2.2	0.2	2.4
	110	51	0.00375	0.00037	0.00193	0.00019	8.2	0.8	9.0
0.0118 gm	120	83	0.00390	0.00061	0.00324	0.00055	13.7	2.3	16.0
each	130	92	0.00270	0.00136	0.00248	0.00125	10.5	5.3	15.8
	140	91	0.00122	0.00247	0.00111	0.00225	4.7	9.5	14.2
	150	81	0.00024	0.00340	0.00019	0.00275	0.8	11.7	12.5
	160	72	0.00013	0.00335	0.00009	0.00241	0.4	10.3	10.7
	170	46	0.00009	0.00251	0.00004	0.00115	0.2	4.9	5.1
	180	38	0.00006	0.00145	0.00002	0.00055	0.1	2.4	2.5
1:2-1/2	100	20	0.00170	0.00075	0.00034	0.00015	1.5	0.6	2.1
	110	45	0.00220	0.00080	0.00099	0.00036	4.4	1.6	6.0
0.0062 gm	120	66	0.00230	0.00112	0.00152	0.00074	6.8	3.3	10.1
CR	130	94	0.00147	0.00202	0.00138	0.00190	6.1	8.5	14.6
0.0156 gm	140	81	0.00075	0.00324	0.00061	0.00263	2.7	11.8	14.5
DE	150	62	0.00036	0.00600	0.00022	0.00372	1.0	16.7	17.7
	160	55	0.00000	0.00618	0.00000	0.00340	0.0	15.2	15.2
	170	46	0.00000	0.00392	0.00000	0.00181	0.0	8.1	8.1
	180	45	0.00000	0.00208	0.00000	0.00093	0.0	4.5	4.5

[a] CR and DE refer to Celanthrene Red 3B and 1,4-Diethyldiamineanthraquinone.

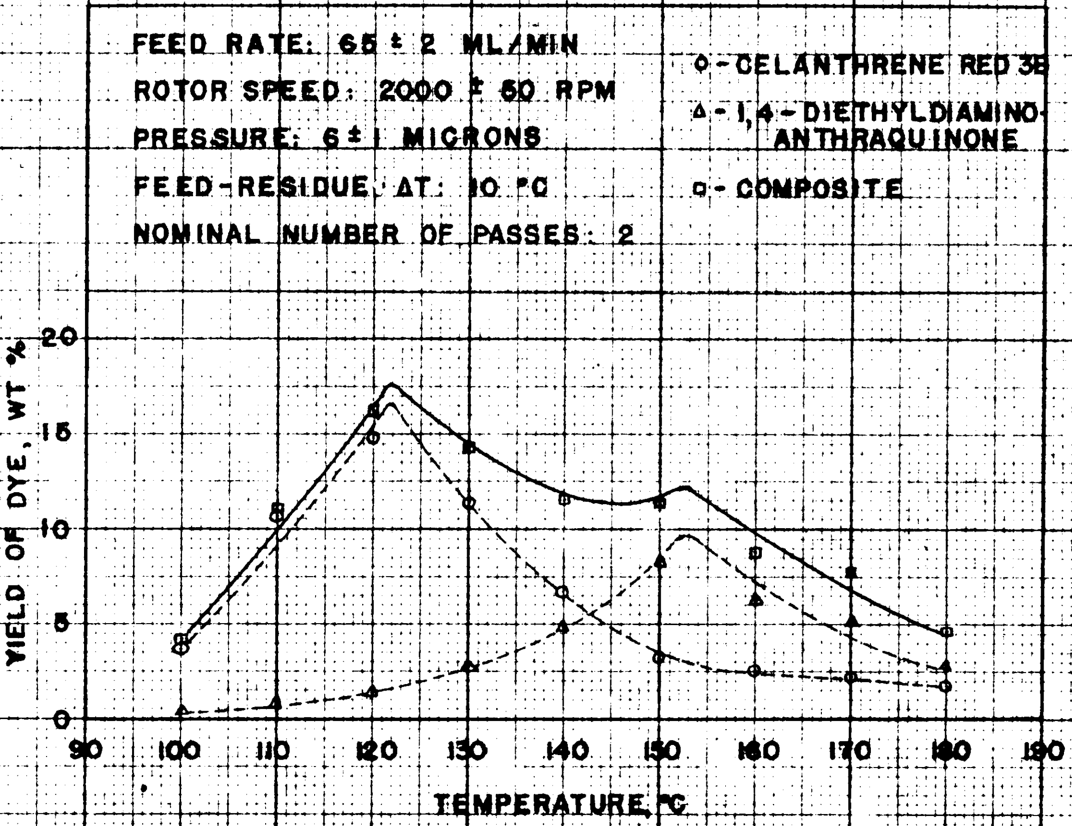


FIGURE 25. MOLECULAR DISTILLATION OF A BINARY MIXTURE OF A 2:1 WEIGHT RATIO OF CELANTHRENE RED 3B TO 1,4-DIETHYLDIAMINOANTHRAQUINONE.

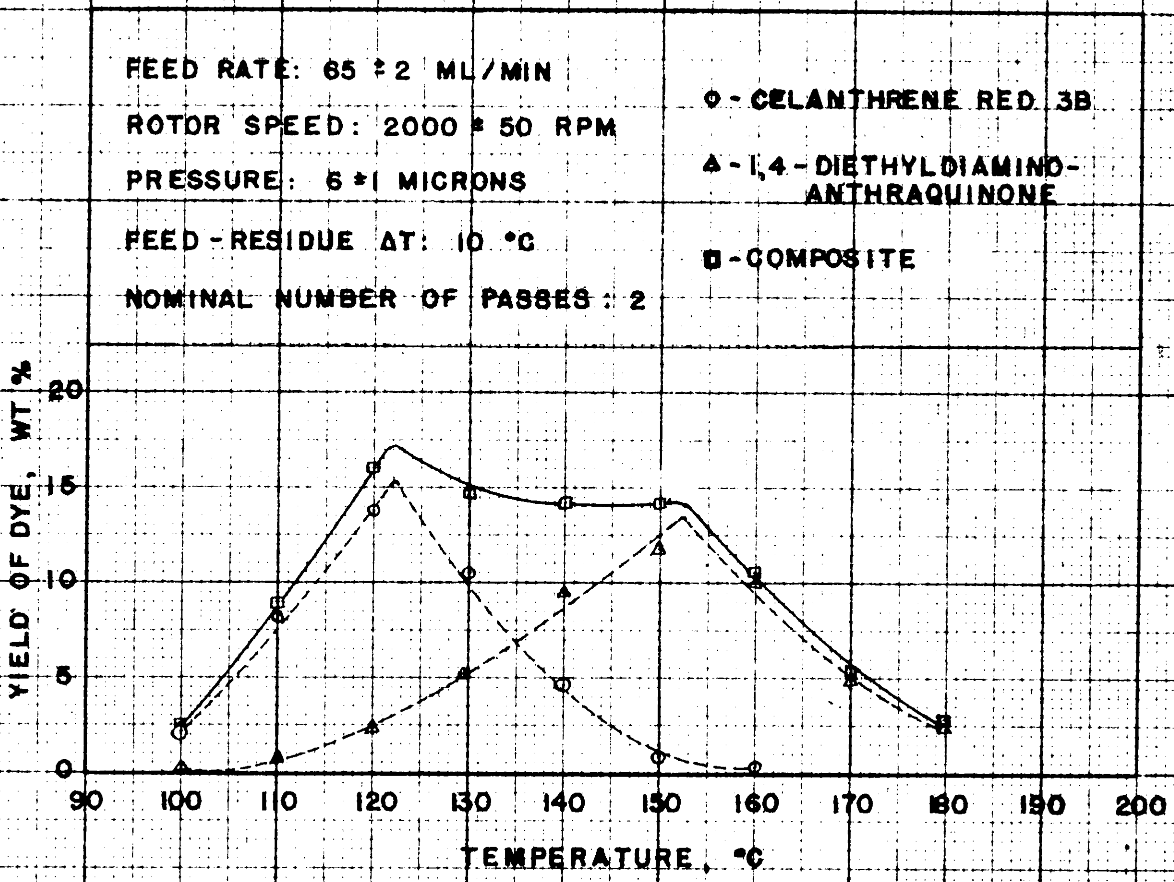


FIGURE 26. MOLECULAR DISTILLATION OF A BINARY MIXTURE OF EQUAL WEIGHTS OF CELANTHRENE RED 3B AND 1,4-DIETHYLDIAMINOANTHRAQUINONE.

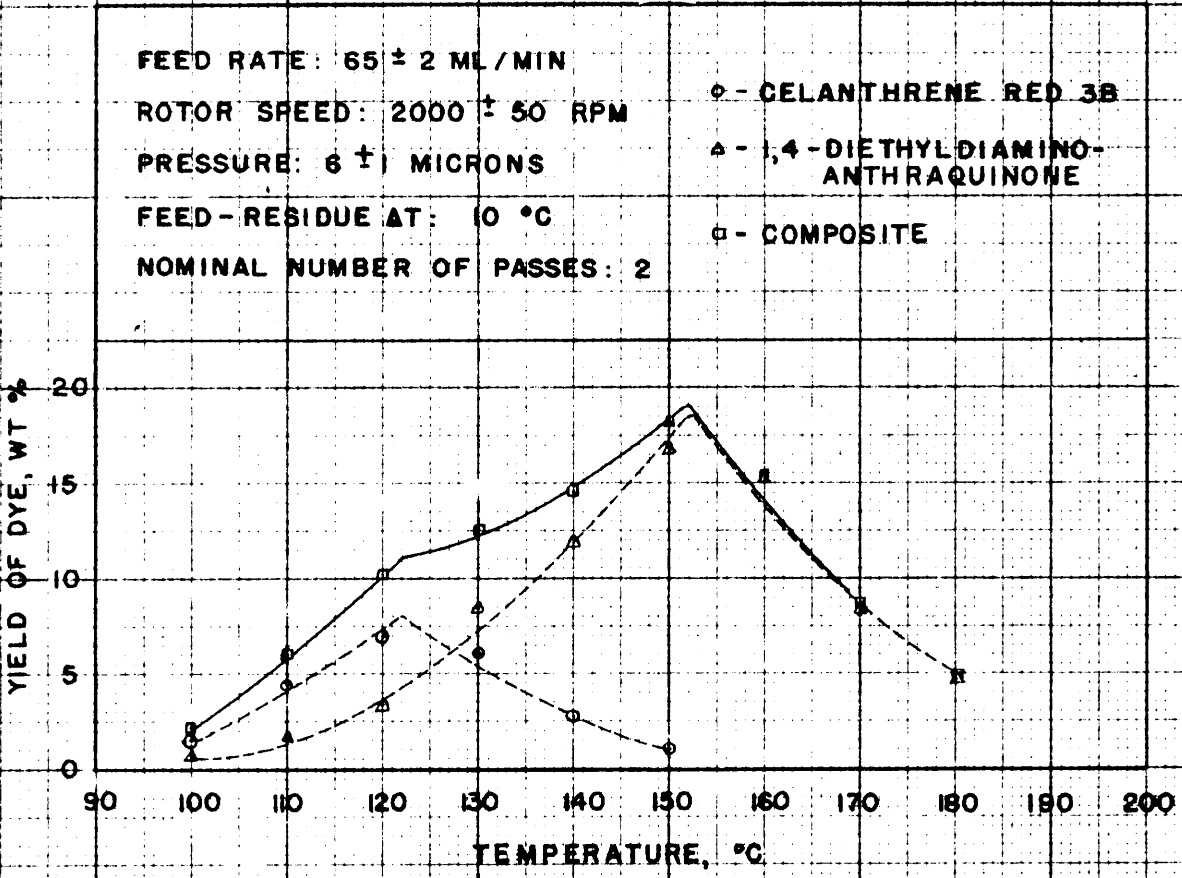


FIGURE 27. MOLECULAR DISTILLATION OF A BINARY MIXTURE OF A 1:2$\frac{1}{2}$ WEIGHT RATIO OF CELANTHRENE RED 3B TO 1,4-DIETHYLDIAMINOANTHRAQUINONE.

TABLE XIV

Data and Results for the Molecular Distillation of a Binary Mixture of Equal Weights of Celanthrene Red 3B and 2,6-Dimethyldiamineanthraquinone Dyes

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 2000 ± 50 rpm
Pressure: 6 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 2
Feed Mixture: 0.0076 gm of each dye

Temperature of Fraction	Volume of Fraction	Concentration of Dye in Fraction		Weight of Dye in Fraction		Yield of Dye in Fraction		
		Celanthrene Red	Dimethyl	Celanthrene Red	Dimethyl	Celanthrene Red	Dimethyl	Composite
°C	ml	gm/100 ml	gm/100 ml	gm	gm	wt %	wt %	wt %
100	20	0.00220	0.00032	0.00044	0.00006	2.9	0.4	3.3
110	46	0.00270	0.00028	0.00124	0.00013	8.5	0.9	9.4
120	71	0.00261	0.00036	0.00185	0.00025	12.2	1.6	13.8
130	78	0.00188	0.00062	0.00147	0.00048	9.7	3.2	12.9
140	86	0.00110	0.00114	0.00094	0.00098	6.2	6.5	12.7
150	70	0.00052	0.00212	0.00036	0.00148	2.4	9.8	12.2
160	64	0.00043	0.00308	0.00028	0.00197	1.8	12.9	14.7
170	47	0.00040	0.00273	0.00019	0.00127	1.2	8.4	9.6
180	34	0.00043	0.00258	0.00014	0.00088	0.9	5.7	6.6

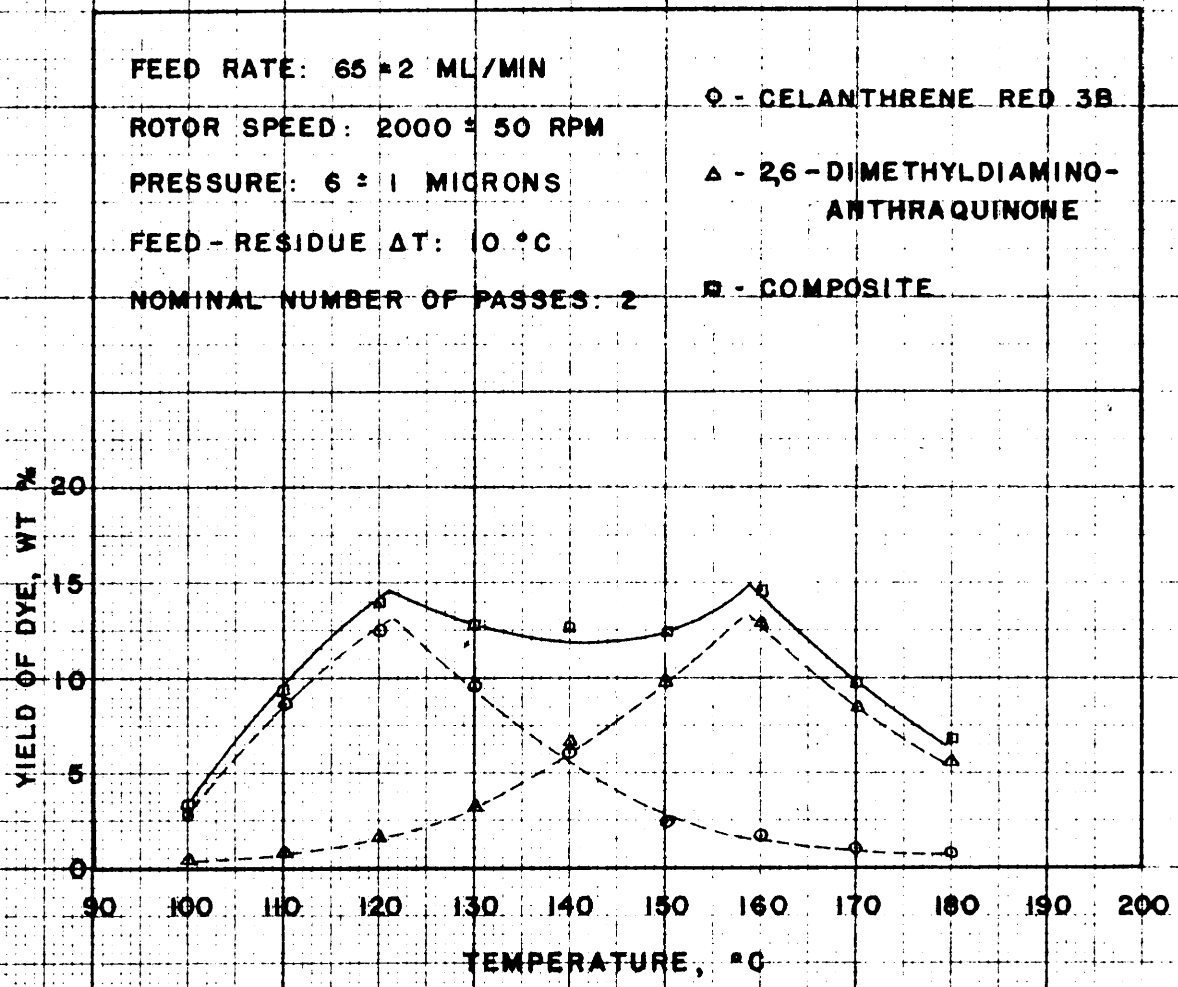


FIGURE 28. MOLECULAR DISTILLATION OF A BINARY MIXTURE OF EQUAL WEIGHTS OF CELANTHRENE RED 3B AND 2,6 DIMETHYLDIAMINOANTHRAQUINONE DYES.

TABLE XV

Data and Results for the Molecular Distillation of a Binary Mixture of Equal Weights of 1,4-Diethyldiamineanthraquinone and 2,6-Dimethyldiamineanthraquinone Dyes

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 2000 ± 50 rpm
Pressure: 6 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 2
Feed Mixture: 0.0082 gm of each dye in 650 ml of heavy mineral oil only

Temperature of Fraction	Volume of Fraction	Concentration of Dye in Fraction		Weight of Dye in Fraction		Yield of Dye in Fraction		
		Diethyl	Dimethyl	Diethyl	Dimethyl	Diethyl	Dimethyl	Composite
°C	ml	gm/100 ml	gm/100 ml	gm	gm	wt %	wt %	wt %
130	45	0.00145	0.00067	0.00065	0.00028	4.0	1.7	5.7
140	63	0.00190	0.00114	0.00120	0.00072	7.3	4.4	11.7
150	85	0.00227	0.00161	0.00193	0.00137	11.8	8.3	20.1
160	87	0.00212	0.00214	0.00184	0.00186	11.2	11.4	22.6
170	85	0.00142	0.00210	0.00121	0.00178	7.4	10.9	18.3
180	100	0.00064	0.00080	0.00064	0.00080	4.0	4.9	8.9
190	56	0.00025	0.00048	0.00014	0.00027	1.5	1.7	3.2

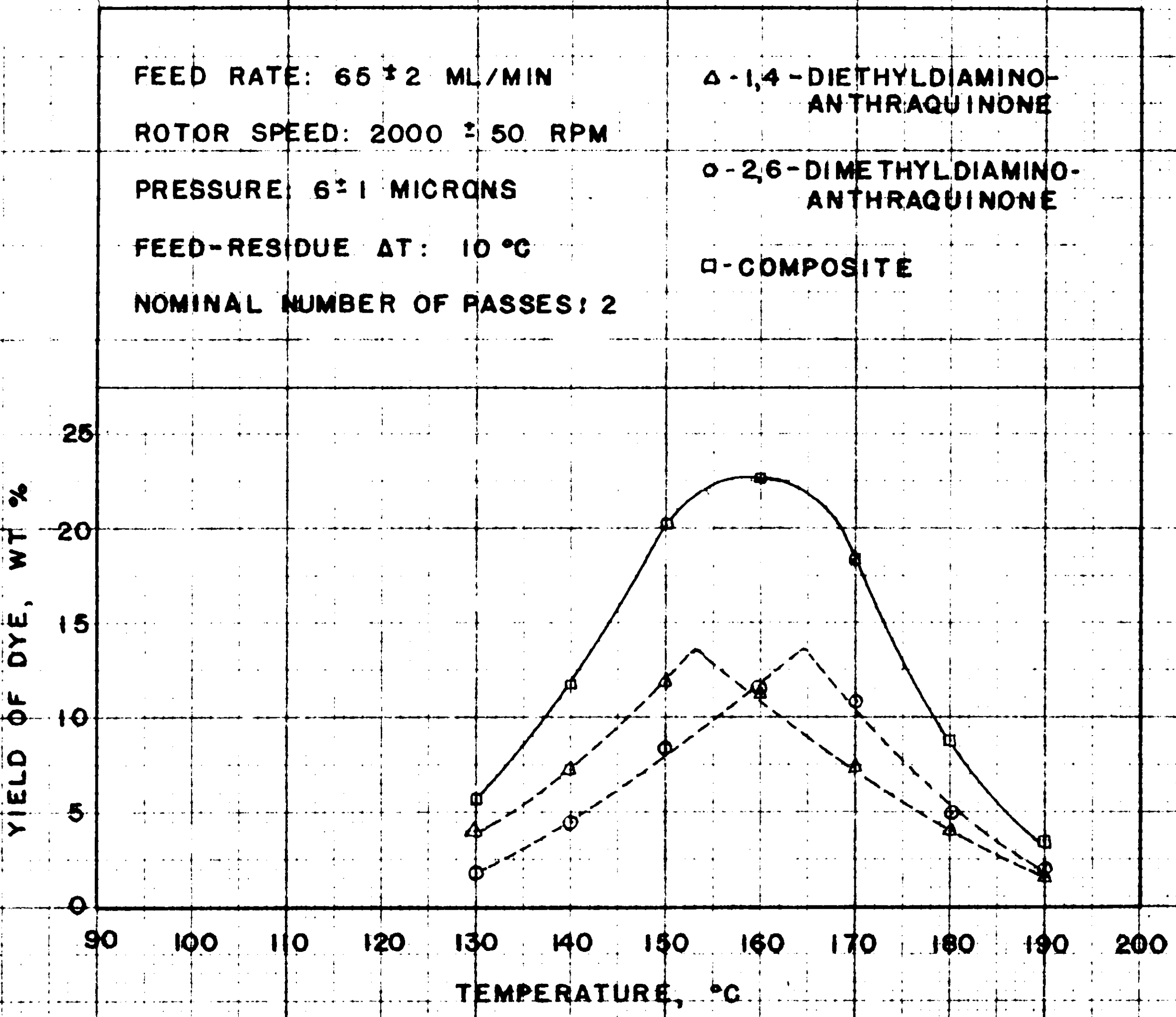


FIGURE 29. MOLECULAR DISTILLATION OF A BINARY MIXTURE OF EQUAL WEIGHTS OF 1,4-DIETHYLDIAMINOANTHRAQUINONE AND 2,6-DIMETHYLDIAMINOANTHRAQUINONE DYES.

TABLE XVI

Data and Results for the Separation of a Binary Mixture of a 2:1 Weight Ratio of Celanthrene Red 3B to 1,4-Diethyldiamineanthraquinone by Extractive Molecular Distillation

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 2000 ± 50 rpm
Pressure: 6 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 2
Original Feed Mixture: 0.0200 gm Celanthrene Red 3B
0.0100 gm 1,4-Diethyldiamineanthraquinone

Type of Distillation	Temperature of Fraction	Volume	Concentration of Dye		Weight of Dye		Yield of Dye		
			CR[a]	DE[a]	CR	DE	CR	DE	Composite
	°C	ml	gm/100 ml	gm/100 ml	gm	gm	wt %	wt %	wt %
Original Distillation[b]	100	26	0.00550	0.00035	0.00110	0.00004	3.7	0.3	4.0
	110	50	0.00648	0.00040	0.00325	0.00020	10.8	0.7	11.5
	120	71	0.00620	0.00061	0.00441	0.00043	14.7	1.4	16.1
	130	73	0.00468	0.00113	0.00342	0.00083	11.4	2.8	14.2
	140	66	0.00305	0.00180	0.00202	0.00143	6.7	4.8	11.5
	150	80	0.00120	0.00308	0.00096	0.00246	3.2	8.2	11.4
	160	57	0.00130	0.00335	0.00074	0.00191	2.5	6.3	8.8
	170	54	0.00130	0.00295	0.00070	0.00159	2.3	5.3	7.6
	180	40	0.00135	0.00190	0.00054	0.00076	1.8	2.5	4.3
Extractive Redistillation[c]	100	16	0.00415	0.00008	0.00067	0.00001	4.2	0.1	4.3
	110	35	0.00538	0.00010	0.00189	0.00003	11.8	0.3	12.1
	120	67	0.00588	0.00015	0.00394	0.00010	24.6	0.7	25.3
	130	78	0.00440	0.00025	0.00343	0.00019	21.4	1.3	22.7
	140	74	0.00270	0.00046	0.00198	0.00034	12.4	2.2	14.6
	150	82	0.00118	0.00083	0.00097	0.00068	6.0	4.3	10.3
	160	69	0.00052	0.00085	0.00036	0.00059	2.3	3.7	6.0
	170	51	0.00038	0.00055	0.00020	0.00028	1.3	1.7	3.0
	180	39	0.00020	0.00024	0.00008	0.00009	0.5	0.6	1.1

[a] CR and DE refer to Celanthrene Red 3B and 1,4-Diethyldiamineanthraquinone.

[b] Original distillation refers to the molecular distillation of the original feed mixture.

[c] Extractive redistillation refers to the distillation of the cumulative volumes of the 100, 110, 120, 130, and 140 °C fractions from the original distillation to which was added 340 ml of heavy mineral oil for a total feed volume of 600 ml.

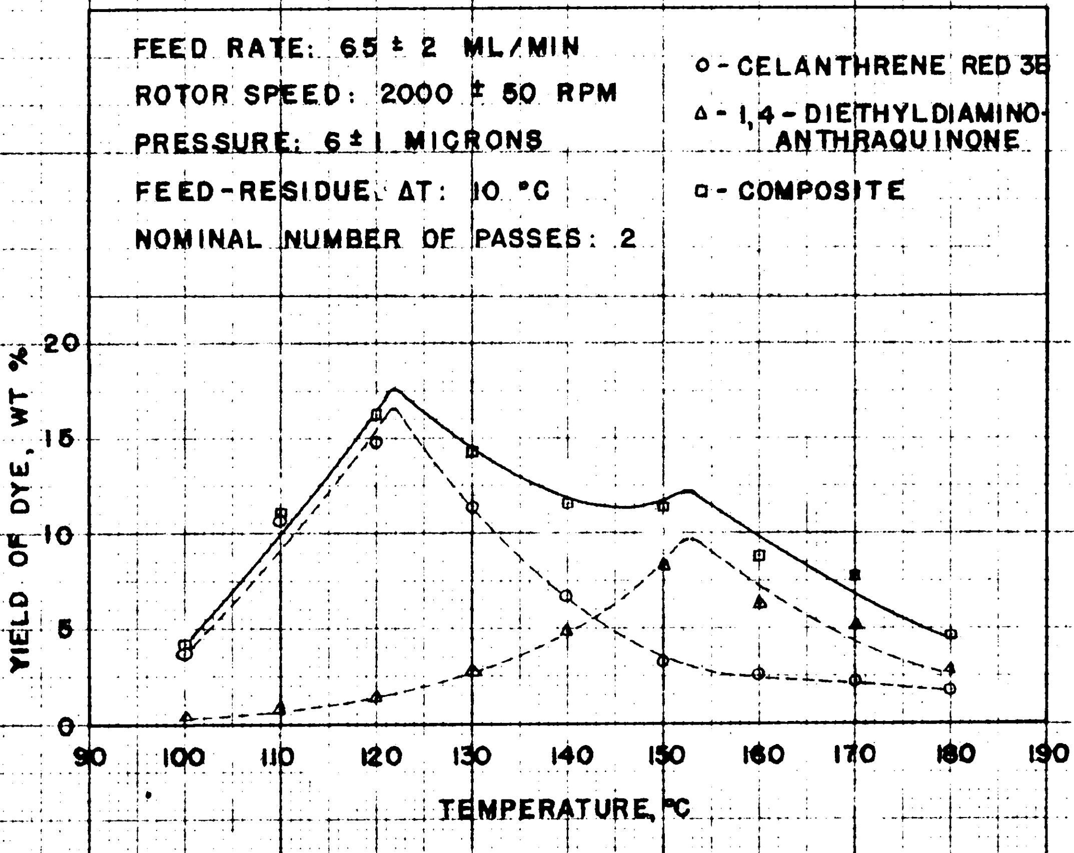


FIGURE 30A. MOLECULAR DISTILLATION OF A BINARY MIXTURE OF A 2:1 WEIGHT RATIO OF CELANTHRENE RED 3B TO 1,4-DIETHYLDIAMINOANTHRAQUINONE.

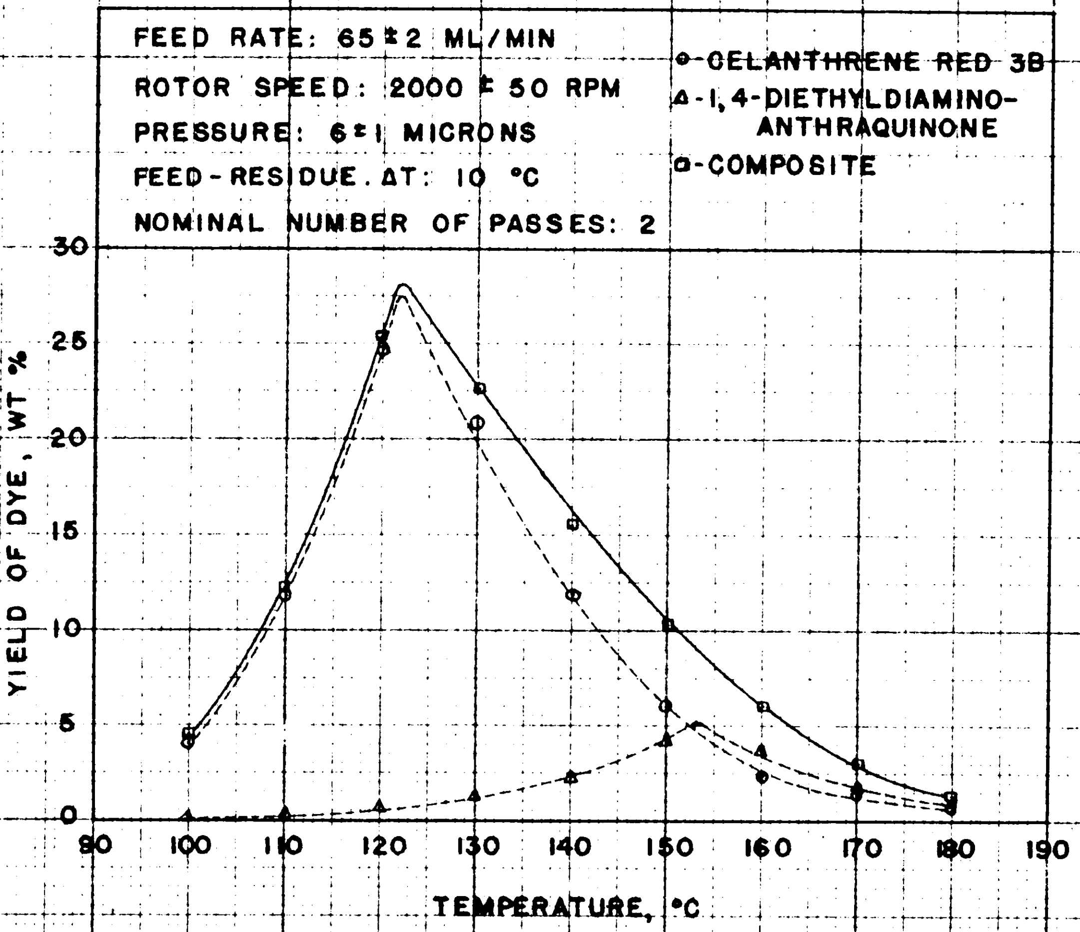


FIGURE 30B. EXTRACTIVE REDISTILLATION OF THE CUMULATIVE FRACTIONS UP TO AND INCLUDING 140 DEGREES CENTIGRADE OBTAINED FROM THE DISTILLATION OF A BINARY MIXTURE OF A 2:1 WEIGHT RATIO OF CELANTHRENE RED 3B TO 1,4-DIETHYLDIAMINOANTHRAQUINONE.

TABLE XVII

Data and Results for the Separation of a Binary Mixture of Equal Weights of Celanthrene Red 3B and 1,4-Diethyldiaminoanthraquinone by Molecular Redistillation

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 2000 ± 50 rpm
Pressure: 6 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 2

Type of Distillation	Temperature of Fraction	Volume	Concentration of Dye		Weight of Dye		Yield of Dye		
			CR [a]	DE [a]	CR	DE	CR	DE	Composite
	°C	ml	gm/100 ml	gm/100 ml	gm	gm	wt %	wt %	wt %
Original Distillation[b]	100	19	0.00289	0.00023	0.00055	0.00004	2.2	0.2	2.4
	110	51	0.00375	0.00037	0.00193	0.00019	8.2	0.8	9.0
	120	83	0.00390	0.00061	0.00324	0.00055	13.7	2.3	16.0
	130	92	0.00270	0.00136	0.00248	0.00125	10.5	5.3	15.8
	140	91	0.00122	0.00247	0.00111	0.00225	4.7	9.5	14.2
	150	81	0.00024	0.00340	0.00019	0.00275	0.8	11.7	12.5
	160	72	0.00013	0.00335	0.00009	0.00241	0.4	10.3	10.7
	170	46	0.00009	0.00251	0.00004	0.00115	0.2	4.9	5.1
	180	38	0.00006	0.00145	0.00002	0.00055	0.1	2.4	2.5
Original Distillation	100	20	0.00280	0.00021	0.00056	0.00004	2.4	0.2	2.6
	110	54	0.00360	0.00035	0.00195	0.00019	8.3	0.8	9.1
	120	85	0.00370	0.00056	0.00316	0.00048	13.4	2.1	15.5
	130	100	0.00221	0.00140	0.00221	0.00140	9.4	5.9	15.3
	140	98	0.00090	0.00247	0.00089	0.00242	3.8	10.5	15.3
	150	82	0.00023	0.00335	0.00017	0.00274	0.7	11.6	12.3
	160	54	0.00004	0.00335	0.00002	0.00198	0.1	8.4	8.5
	170	47	0.00004	0.00251	0.00002	0.00112	0.1	4.7	4.8
	180	43	0.00004	0.00130	0.00002	0.00056	0.1	2.4	2.5
First Redistillation[c]	100	35	0.00330	0.00011	0.00115	0.00004	5.4	0.2	5.6
	110	67	0.00410	0.00016	0.00274	0.00011	12.7	0.5	13.2
	120	107	0.00430	0.00025	0.00460	0.00026	21.4	1.3	22.7
	130	118	0.00310	0.00052	0.00366	0.00062	17.0	2.9	19.9
	140	101	0.00038	0.00117	0.00038	0.00118	1.8	5.5	7.3
	150	72	0.00020	0.00225	0.00014	0.00162	0.6	7.5	8.1
Second Redistillation[d]	100	26	0.00287	0.00006	0.00075	0.00001	5.1	0.1	5.2
	110	74	0.00388	0.00010	0.00287	0.00007	19.7	0.5	20.2
	120	92	0.00393	0.00016	0.00362	0.00015	24.8	1.0	25.8
	130	89	0.00310	0.00030	0.00276	0.00026	18.9	1.8	20.7
	140	50	0.00160	0.00088	0.00080	0.00044	5.5	3.0	8.5

[a] CR and DE refer to Celanthrene Red 3B and 1,4-Diethyldiaminoanthraquinone.

[b] Original Distillations are the distillations of the equal weight binary mixtures.

[c] First Redistillation is distillation of the cumulative volumes up to and including the 140 °C fractions of the duplicate original distillations.

[d] Second Redistillation is distillation of the cumulative fractions from the first redistillation up to the 140 °C fraction.

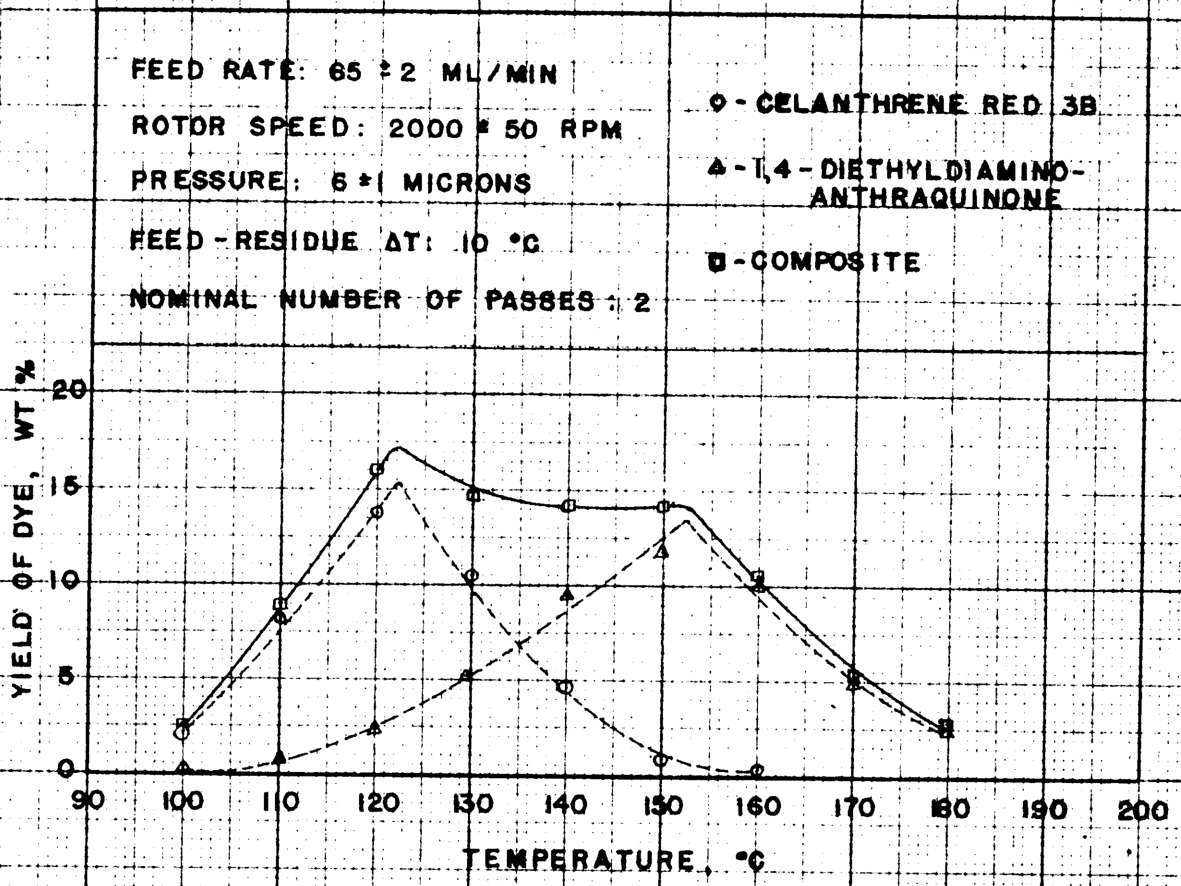


FIGURE 31A. MOLECULAR DISTILLATION OF A BINARY MIXTURE OF EQUAL WEIGHTS OF CELANTHRENE RED 3B AND 1,4-DIETHYLDIAMINOANTHRAQUINONE.

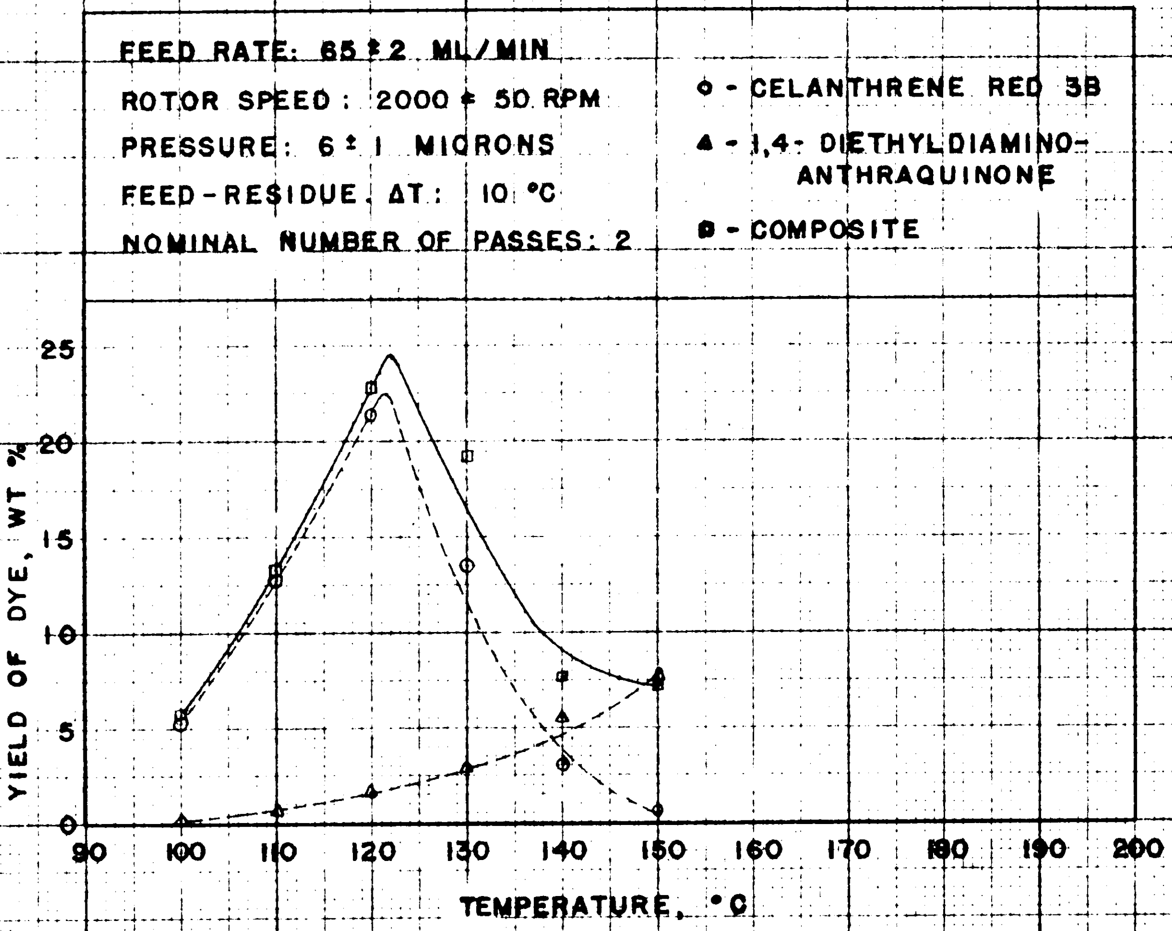


FIGURE 31B. REDISTILLATION OF THE CUMULATIVE FRACTIONS UP TO 140 DEGREES CENTIGRADE OBTAINED FROM THE DISTILLATION OF A BINARY MIXTURE OF EQUAL WEIGHTS OF CELANTHRENE RED 3B AND 1,4-DIETHYLDIAMINOANTHRAQUINONE.

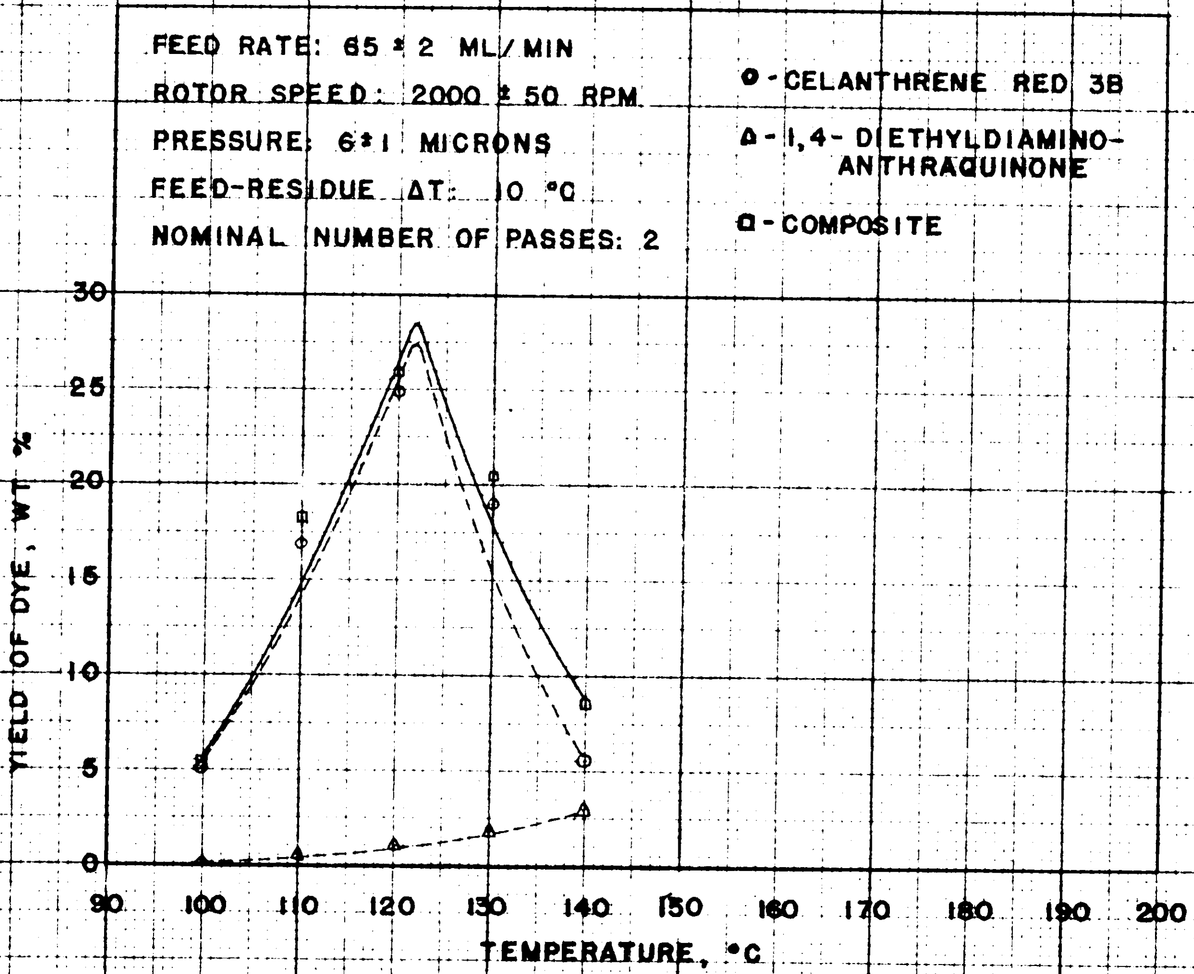


FIGURE 31C. REDISTILLATION OF THE CUMULATIVE FRACTIONS UP TO 140 DEGREES CENTIGRADE OBTAINED FROM THE REDISTILLATION OF A BINARY MIXTURE OF EQUAL WEIGHTS OF CELANTHRENE RED 3B AND 1,4-DIETHYLDIAMINOANTHRAQUINONE.

TABLE XVIII

Data and Results for the Molecular Distillation of a Tertiary Mixture of Equal Weights of Celanthrene Red 3B, 1,4-Diethyldiaminoanthraquinone, and 2,6-Dimethyldiaminoanthraquinone Dyes

Feed Rate: 65 ± 2 ml/min
Rotor Speed: 2000 ± 50 rpm
Pressure: 6 ± 1 microns
Feed-Residue ΔT: 10 °C
Nominal Number of Passes: 2
Feed Mixture: 0.0071 gm of each dye

Temperature of Fraction	Volume	Concentration of Dye in Fraction			Weight of Dye in Fraction			Yield of Dye in Fraction			
		CR[a]	DE[a]	DM[a]	CR	DE	DM	CR	DE	DM	Comp.
°C	ml	gm/100 ml	gm/100 ml	gm/100 ml	gm	gm	gm	wt %	wt %	wt %	wt %
100	25	0.00240	0.00018	0.00011	0.00060	0.00003	0.00003	2.8	0.1	0.1	3.0
110	60	0.00250	0.00032	0.00016	0.00150	0.00019	0.00010	7.1	0.9	0.5	8.5
120	80	0.00250	0.00055	0.00026	0.00200	0.00044	0.00021	9.4	2.1	1.0	12.5
130	70	0.00150	0.00088	0.00055	0.00105	0.00062	0.00039	5.0	2.9	1.8	9.7
140	80	0.00070	0.00164	0.00120	0.00056	0.00131	0.00096	2.6	6.2	4.5	13.3
150	77	0.00007	0.00230	0.00218	0.00005	0.00177	0.00167	0.2	8.3	7.9	16.4
160	61	0.00000	0.00220	0.00289	0.00000	0.00134	0.00177	0.0	6.3	8.3	14.6
170	44	0.00000	0.00133	0.00248	0.00000	0.00059	0.00109	0.0	2.8	5.1	7.9
180	37	0.00000	0.00050	0.00183	0.00000	0.00019	0.00068	0.0	0.9	3.2	4.1

[a] CR, DE, and DM refer to Celanthrene Red 3B, 1,4-Diethyldiaminoanthraquinone, and 2,6-Dimethyldiaminoanthraquinone.

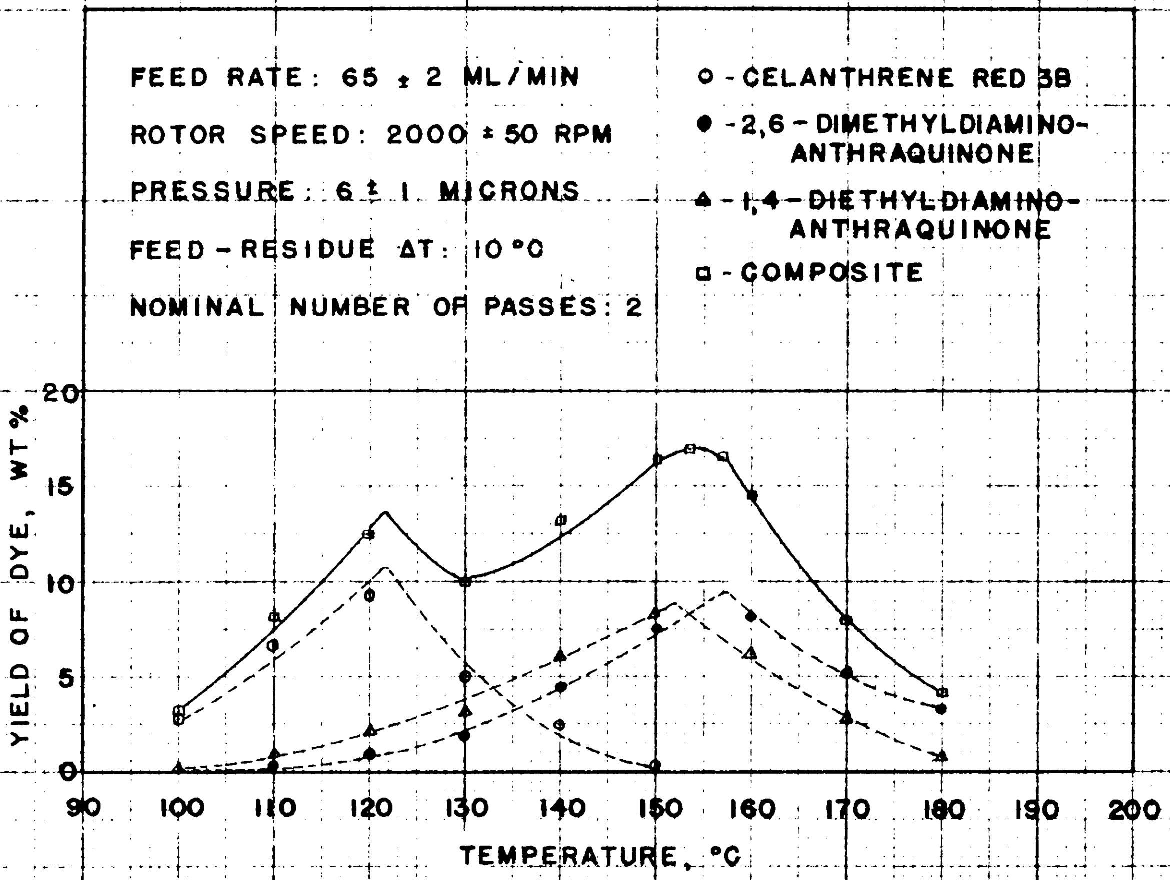


FIGURE 32. MOLECULAR DISTILLATION OF A TERTIARY MIXTURE OF EQUAL WEIGHTS OF CELANTHRENE RED 3B, 1,4-DIETHYL- AND 2,6-DIMETHYL-DIAMINOANTHRAQUINONE DYES.

IV. DISCUSSION

In order to study the molecular distillation of various anthraquinone dyes, a series of tests was made on a laboratory centrifugal molecular still. The results of the investigation are discussed, recommendations are made for future studies, and the limitations of the experimentation are presented.

Discussion of Results

The discussion of results will consider the various results obtained during the investigation and several of the operational features of the redesigned molecular still.

Constant-Yield Oil. A solvent was required for the various anthraquinone dyes which would distill with the dyes and provide drainage of the potent substance from the bell jar condensing surface.

Colorless Constant-Yield Oil. In order to analyze the dye concentration in the distilling fractions by colorimetric means, it was desirable to use a colorless oil. Attempts were made to decolorize straw-colored oils such as Essolube No 7 motor oil, Teresso 52, and Conco hyvac oil with decolorizing carbon. The use of decolorizing carbon in hot oil (up to 250 degrees Centigrade) resulted in an oil slightly lighter but still yellow-orange in color and not satisfactory for use as distillation would have resulted in fractions of oil which would have varied from nearly colorless to dark red in color. Any attempt to standardise the analytical technique using the colorimeter would have resulted in a great deal of error which would have made the investigation valueless. Colorless light and extra heavy grades of mineral oil were then studied for use as a constant-yield oil.

Molecular Distillation of Constant-Yield Oil. Numerous distillations of both light and heavy mineral oils were made to study the constancy of the yields of mineral oil for each temperature of distillation. Table VII, page 175, gives two typical tests for each grade of oil as distilled with fractions collected continuously over 10-degree temperature intervals. It was originally planned that equal volumes of oil from each fraction would be blended to form a constant-yield oil; it being expected that the volume that had once come over at one temperature would distill at the same temperature when used as constant-yield oil. This was not the case, however, as can be evidenced from a study of Table X, page 179, for the distillation of 1,4-diethyldiaminoanthraquinone using the continuous temperature rise technique as had been used in the preparation of the supposedly "constant-yield" oil. Forty milliliters of oil from each of the 10 fractions from 80 to 180 degrees Centigrade were used as the solvent for the dye for a total volume of 400 milliliters. Distillation of the dye solution gave yields varying from 25.0 to 62.0 milliliters for the first eight fractions with a residue of 74 milliliters left after the distillation of of the 150 - 160 degree fraction. It was evident that the "constant-yield" oil produced by mixing equal volumes of each fraction from previous distillations would not give yields which would be sufficiently constant. It was further evident that a more nearly "constant-yield" oil could be produced by merely mixing light and heavy mineral oils in proportions such that the yields which resulted would be of approximately the same volume. The light mineral oil would provide the lower fractions in larger quantity and the heavy mineral oil, the higher fractions.

Further tests, however, were made with a discontinuous temperature rise technique; the reason for which will be discussed further in a later section. Table VIII, page 176, shows the distillation of two duplicate batches of mixed oils in the volume ratio of 8:7 of heavy mineral oil to light mineral oil. The same conditions of operation were used as in all subsequent tests except for a rotor speed of 1720 rather than 2000 revolutions per minute and a pressure of 2 microns rather than 6 microns. The result of these exceptions is minor as determined by Bull(7, 8) and as will be discussed in a later section. It can be seen that with the exception of the 100 and 180-degree fractions, the first and last fractions of the temperature range studied, the yields are fairly constant varying from 71 to 92 milliliters for Test 1 and from 63 to 92 milliliters for Test 2. As expected, the 100 and 180-degree fractions were much smaller, 34 and 26 milliliters for Test 1 and 30 and 33 milliliters for Test 2. It is believed that the error caused by the smaller yields and therefore less drainage for these fractions was small since the dyes employed distilled only in small amounts, not over 10 per cent by weight and generally less than 4 or 5 per cent, at these temperatures in the tests made.

It will be further noticed from Table VIII, page 176, that over 100 milliliters of oil remained in the residue and served as carrier oil which did not distill at the temperature range employed in the study. Since the holdup in the lines of the still was approximately 50 milliliters, this residue was necessary to permit distillation at the higher temperatures employed when the distilland was reduced drastically from the original volume.

Colorimeter Readings of Constant-Yield Oil Fractions. Although all were colorless, the various fractions obtained from the distillation of the light and heavy mineral oil mixtures gave slightly different colorimeter readings. In order that the difference in readings be taken into account to eliminate error in dye analysis, the various constant-yield oil fractions were analyzed using the colorimeter and the various filters employed in the analysis. Table IX, page 177, gives the readings obtained for the various fractions.

Indication of Thermal Decomposition of Mineral Oil. The colorimeter readings for the fractions of the constant-yield oil are of interest since they point out the possibility of slight decomposition taking place during distillation. The readings were made with light mineral oil as the zero or blank reading. Heavy mineral oil gave a reading of 11 using the blue filter against a zero reading for light mineral oil. It would be expected therefore that some readings would be negative and that the average reading would be about 5 or 6. Such was not the case. Readings as seen in Table IX, page 177, varied from 2 to 20 for the 90 to the 190-degree Centigrade fractions. It was supposed that some slight decomposition took place in the mineral oil when heated on the rotor and

and that this thermal decomposition increased as the temperature increased. This decomposition in itself caused little or no error in the analysis of the dye fractions since the colorimeter corrections were made. It does point out that some danger probably still exists from thermal decomposition and that the anthraquinone dyes may have suffered some similar decomposition on distillation.

Continuous Temperature Rise Technique. It soon became evident after the performance of several distillations using the molecular still that a rigorously standardized procedure would have to be developed and followed throughout the tests if comparable results were to be obtained. The development of such a technique is of especial interest.

It was originally planned to collect the various fractions during distillation while the temperature was raised slowly over the fraction interval. For instance, while the temperature of the residue was raised from 100 to 110 degrees Centigrade by addition of heat on the rotor, the distillate was collected. When the residue temperature reached 110 degrees Centigrade, the complete fraction was considered collected and removed from the collection tank and the collection of the next fraction, the 110-120 degree fraction, was begun. No consideration was made for the time required to raise the temperature each of the 10-degree intervals from 90 to 180 degrees Centigrade, the general range of distillation except that there was made a relatively unsuccessful attempt to raise the temperature approximately one degree Centigrade every five minutes for both the feed and the residue. The bulk of metal making up the rotor heated and cooled so slowly that control of the temperature of the residue during heating was poor although the temperature could be held constant at any desired level when once attained.

The other conditions of distillation were held constant: pressure of 2 ± 1 microns, difference between feed and residue temperatures of 10 degrees Centigrade, rotor speed of 1720 ± 5 revolutions per minute, and feed rate of 122 ± 3 milliliters per minute.

The time required to raise the temperature varied greatly from fraction to fraction within one distillation and for the same fraction in the several distillations made using this continuous temperature rise technique as evidenced from a study of Tables VII and X, pages 175 and 179. Table VII, for the distillation of light and heavy mineral oils, best illustrates the varying collection times and their apparent effect on the fraction volume collected. The two tests on light mineral oil employed collection times which varied less than usual, from 55 to 65 minutes for each fraction with this 10-minute difference being the greatest for any one fraction. The slight but apparent effect of increased collection (distillation) time is evident, however, as the test in which each fraction received the longer time gave the greater yield. For instance, for the 120-130 degree fraction, Test 1 and Test 2 with collection times of 65 and 55 minutes gave yields of 115 and 105 milliliters of oil, respectively. The error which would have resulted from the use of this continuous temperature rise technique without most exacting control of the collection time is further illustrated in Table VII by the two tests on heavy mineral oil. Collection times varied from 30 to 60 minutes with the greatest difference in collection time for the same fraction in the two tests being 20 minutes for three of the eight fractions collected. Yields for similar fractions with differences in volumes of as much as 18 milliliters were observed.

Distillation of Anthraquinone Dyes by Continuous Temperature Rise Technique. Table X, page 179, gives the data and results for the distillation of 1,4-diethyldiaminoanthraquinone, 1,4-diisopropyldiaminoanthraquinone, and 1,4-dibutyldiaminoanthraquinone by the continuous temperature rise technique. Collection times for the various fractions varied from 35 to 125 minutes for 1,4-diethyldiaminoanthraquinone, from 30 to 110 minutes for 1,4-diisopropyldiaminoanthraquinone, and from 30 to 100 minutes for 1,4-dibutyldiaminoanthraquinone. The volumes of oil solvent in these three distillations varied from 400 milliliters for the test with 1,4-diethyldiaminoanthraquinone to 700 milliliters for 1,4-dibutyldiaminoanthraquinone. For this reason, a consideration of the effect of collection times on fraction volumes is not as valid as in the distillation of light and heavy mineral oils discussed previously where similar feed volumes were employed.

The distillations are of further interest, however. It will be noted from Table X, page 179, and Figure 19, page 180, that the elimination maxima for 1,4-diethyldiaminoanthraquinone, 1,4-diisopropyldiaminoanthraquinone, and 1,4-dibutyldiaminoanthraquinone were 131, 141, and 152 degrees Centigrade, respectively. Hickman(45), who determined the maxima for these dyes as 153, 162, and 171 degrees Centigrade, called attention to the apparent increase of approximately 10 degrees in the elimination maximum by the addition of two CH_2 groups to the anthraquinone side chain. He suggested that this difference would not change significantly even if a different method of procedure in the distillation resulted in an increase or decrease of the temperature of the elimination maxima. This has apparently been the case in this investigation with differences of 10 and 11 degrees between the succeeding members of the homologous series compared to the 9-degree differences found by Hickman.

Despite the general agreement of the elimination maxima for the three dyes with expected results, it was felt that duplication of results by the continuous temperature rise technique would be difficult if not impossible with the irregular heating which resulted from the available temperature control. Therefore, a method of discontinuous temperature rise distillation was devised.

Discontinuous Temperature Rise Technique. Rather than collecting the distillate during the rise in temperature as in the continuous temperature rise technique, the distillate fractions were collected only after the feed and residue had been brought to and steadily maintained at the desired temperature. In order to standardize the time allowed for distillation at each temperature, the number of passes of the feed over the rotor was set at five nominal passes. A nominal pass was considered to be one pass of the entire feed over the rotor. In determining the amount of time required for five passes, only the initial volume before the first pass was considered for each fraction and the time alloted was that for five passes of this volume. It is acknowledged that each pass would result in some distillation and that the feed volume would thus be decreased by each successive pass. This, of course, resulted in a somewhat greater number of passes than five and, hence, the use of the term, "nominal passes". Since this procedure was used for each fraction collected, the operation was considered as standardised. The use of the same mineral oil mixture as the dye solvent resulted in volumes of feed for each temperature being approximately equal from test to test. The time of distillation for the same fraction in different distillations was thereby held reasonably constant.

Distillation of Various Anthraquinone Dyes Using the Discontinuous Temperature Rise Technique. Celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone were distilled employing the discontinuous temperature rise technique with five nominal passes of the feed over the rotor. The data and results are shown in Table XI, page 181, and the elimination curves appear in Figure 20, page 182. Elimination maxima of 115, 151, and 154 degrees Centigrade were obtained for celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone, respectively. According to Hickman(45), the elimination maximum for dimethyldiaminoanthraquinone should have been approximately 10 degrees Centigrade below that of diethyldiaminoanthraquinone, or about 141 degrees Centigrade for this case where 151 degrees Centigrade was found to be the elimination maximum for diethyldiaminoanthraquinone. The elimination maximum for 2,6-dimethyldiaminoanthraquinone was found to be 154 degrees Centigrade, however, 13 degrees above that expected and three degrees higher than the maximum for 1,4-diethyldiaminoanthraquinone. The only explanation appears to be in the location of the sidechains on the anthraquinone molecule in the 2,6 position rather than in the 1,4 position. No mention is made in the literature of the effect of the sidechain. That error might have caused this result is not likely as succeeding tests which will be discussed further substantiated the fact that the elimination maximum of 2,6-dimethyldiaminoanthraquinone is above that of 1,4-diethyldiaminoanthraquinone. The position of the sidechain apparently has a profound effect on the molecular distillation of a substance as well as on the physical and chemical properties.

The distillation of diisopropyldiaminoanthraquinone and dibutyldiaminoanthraquinone with the discontinuous temperature rise technique was not attempted as only one "tail" of the elimination curve would have been obtained over the temperature range for which a mineral oil solvent was available.

Comparison of the Continuous and Discontinuous Techniques. One dye, 1,4-diethyldiaminoanthraquinone, was distilled using both techniques of molecular distillation and can be used for comparison purposes. A change of 20 degrees from 131 to 151 degrees Centigrade was noted for the elimination maximum of the dye. Figure 21, page 183, gives the elimination curves as obtained from the distillations of the dye by the two methods. The elimination curve for the continuous technique is taller and narrower compared to the broader and flatter curve from the discontinuous method. The difference between the two curves emphatically points out the need for a well-standardized technique of molecular distillation if a number of tests are to be compared.

Standardisation of Procedure. In research on the molecular still which progressed concurrently with this investigation, Bull studied the effect of variables such as the nominal number of passes(5), feed rate(6), rotor speed(7), pressure(8), and difference between feed and residue temperature(9). This study is summarized as it affected the standardization of a procedure for the further distillation tests made using the still.

Nominal Number of Passes. The nominal number of passes of the feed over the rotor has a pronounced effect on the elimination of 1,4-diethyldiamineanthraquinone. Bull obtained elimination maxima of 144, 152 and 164 degrees Centigrade for nominal number of passes of 4, 2, and 1, respectively. A taller and narrower curve was obtained as the number of passes was increased.

Feed Rate. Bull studied feed rates of 22, 40, 65, and 100 milliliters per minute and obtained elimination maxima for 1,4-diethyldiaminoanthraquinone of 134, 139, 152, and 158 degrees Centigrade.

Rotor Speed. Bull employed rotor speeds of 1000, 2000, 3000, and 5000 revolutions per minute in individual tests on 1,4-diethyldiaminoanthraquinone and noted no effect on either the elimination curve or the elimination maximum of 152 degrees Centigrade.

Pressure. The pressure of operation had a great effect on the distillation of 1,4-diethyldiaminoanthraquinone. Pressures of 2, 6, 25, 50, and 100 microns of mercury, absolute pressure, gave elimination maxima of 148, 152, 158, 173, and 177 degrees Centigrade, respectively.

Difference in Feed and Residue Temperatures. Differences of 10 and 20 degrees Centigrade between the feed and residue temperatures were studied and found to give the same elimination curve and maximum.

Choice of Conditions for Standardised Technique and Variations in these Conditions During Subsequent Distillations. The operating conditions chosen for a standardised technique were 2 nominal passes, 65 milliliters per minute feed rate, 2000 revolutions per minute rotor speed, 6 microns pressure, and a 10-degree Centigrade difference between the feed and residue temperatures.

Two nominal passes of the feed over the rotor were chosen because this provided adequate distillation times for all fractions (varied from approximately 20 minutes for first fraction to approximately 4 minutes for last fraction) without unreasonably long first and second fraction times up to 40 minutes which would have been required for 4 nominal passes. The use of one nominal pass was seriously considered but the idea abandoned because it was felt that two passes would result in less experimental error and more equal distillation times for the same fraction in various tests. It is estimated that from 2.1 to 2.4 actual passes of the feed over the rotor were made for the various fractions from the previously discussed definition of the "nominal" pass.

A feed rate of 65 milliliters per minute was used as this was the most easily maintained feed rate which provided a rather uniform flow of feed to the rotor and was sufficient to insure a layer over the entire rotor surface at all times. The feed rate varied slightly during the tests probably due to some viscosity variation as the temperature rose and the lower-distilling, less-viscous oil was distilled over. The feed rate was changed when necessary to maintain the rate at 65 ± 2 milliliters per minute. It is believed that the slight variation of the feed rate did not result in any error greater than the normal experimental error if a feed rate of exactly 65 milliliters per minute could have been maintained.

Although the rotor speed was found to have no apparent effect on distillation within a range from 1000 to 5000 revolutions per minute, a rotor speed of 2000 revolutions per minute was chosen arbitrarily and maintained constant to ±50 revolutions per minute.

A pressure of six microns of mercury, absolute, was used in the tests since this pressure was the lowest obtainable with the reconstructed system when the motor drive was enclosed in the vacuum chamber. The pressure varied from 5 to 7 microns which was not believed to be sufficient variation to affect the results obtained. At a pressure of six microns, the mean free path calculated for the gas molecules was 3.5 centimeters. The gap between the rotor and the bell jar condensing surface can be approximated as being an average of 6.5 centimeters, 1.85 times the mean free path.

The feed temperature was maintained 10 degrees Centigrade below the residue temperature. At temperatures less than 7 degrees from the residue temperature, flashing was evident.

Temperature differences greater than 10 degrees were more difficult to maintain constant. A 10-degree temperature difference was relatively easy to maintain constant with variations in the temperatures not greater than ±1/2 degree.

Molecular Distillation of Single Dyes Using the Standardized Technique. Before distillation of binary and tertiary mixtures of the various anthraquinone dyes was attempted, each of the dyes to be used in the mixtures was distilled individually to obtain the elimination curves and maxima. Table XII, page 184, and Figures 22, 23, and 24, pages 185, 186, and 187, give the data and results and elimination curves, respectively, for the distillation of celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone.

Celanthrene Red 3B. Three tests were made on celanthrene red 3B. Two tests were made under standardized conditions and one was made at an absolute pressure of two microns rather than at six microns. In this test at the lower pressure, all other conditions; feed rate, rotor speed, nominal number of passes, and difference between feed and residue temperature; were similar to the standard conditions. Therefore, the effect of the pressure on the distillation of celanthrene red 3B is noted in a shift of the elimination maximum from 113 to 121 degrees Centigrade with a change in the pressure from 2 to 6 microns. This pressure effect is somewhat greater than observed by Bull(8) for diethyldiaminoanthraquinone where the elimination maximum shifted from 148 to 152 degrees Centigrade for a similar change in pressure.

The duplicate tests made on celanthrene red 3B give an indication of the ability to duplicate results under a standardized procedure of operation of the molecular still. The dye yields of the fractions for the second test varied by only -0.4, -0.2, 0.8, 1.2, 1.8, 0.2, and 0.6 weight per cent for the 100 through the 160-degree fractions from the first test and a similar elimination maximum of 121 degrees Centigrade was obtained for both distillations. Variations of less than 2 or 3 weight per cent were considered as being within the bounds of normal experimental error from minor drainage error, colorimeter reading and analysis error, and other minor sources of error.

1,4-Diethyldiaminoanthraquinone. Duplicate tests were made for 1,4-diethyldiaminoanthraquinone as for celanthrene red 3B with an elimination maximum of 152 degrees Centigrade for both tests with variations in the yield for similar fractions less than 3.0 per cent except for the 170-degree fraction which varied by 4.6 weight per cent.

2,6-Dimethyldiaminoanthraquinone. The elimination maximum was found to be 159 degrees Centigrade under distillation using standardized conditions.

Comparison of Results of Standardized Technique with Discontinuous Temperature Rise Technique. The standardized technique used was similar to the discontinuous technique except for the choice of operating conditions. It is interesting to compare the results of the tests for the three anthraquinone dyes distilled by both methods. All the conditions were changed somewhat with the feed rate being 65 instead of 122 milliliters per minute for the standardized technique, the rotor speed being 2000 rather than 1720 revolutions per minute, the nominal number of passes being 2 instead of 5, and the pressure being 6 instead of 2 microns. Elimination maxima were 115, 151, and 154 degrees Centigrade for the discontinuous technique compared to 121, 152, and 159 degrees Centigrade for the standardized technique for celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone, respectively. The elimination maxima shifted 6, 1, and 5 degrees for the three dyes. Hickman(43) has stated that changes in the operating conditions will shift the maximum of each substance being studied by an amount such that the relative separation of the maxima remains approximately constant. This has apparently been the case in the distillation of the three dyes under two different sets of operating conditions. The possible exception, 1,4-diethyldiaminoanthraquinone, where the elimination maximum shifted only one degree instead of five or six degrees would be difficult to explain other than by experimental error. An elimination maximum of 155 or 156 degrees Centigrade might have been expected. However, as discussed previously, duplicate tests gave a similar maximum of 152 degrees for this dye when distilled using the standardized technique. It is likely that some error in the discontinuous technique may have resulted in an elimination maximum by this procedure that was four or five degrees too high (151 rather than 147 or 148 degrees Centigrade which would have been consistent with the other results). Since only one test was made using 1,4-diethyldiaminoanthraquinone by the discontinuous technique, error might easily have been present in this test. Hickman(43) further suggests that his theory may not hold where substances have widely different latent heats. Since all three dyes studied were members of the same series of dyes, it is believed that the latent heats did not differ sufficiently to effect such results.

Molecular Distillation of Binary Mixtures of Dyes. The three dyes distilled singly were employed in the study of the distillation of binary mixtures with elimination maxima both fairly close together and relatively far apart as well as to study the effect of varying weight ratios of the dyes in binary mixture. With elimination maxima of 121, 152, and 159 degrees Centigrade for celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone, respectively, it was possible to study binary mixtures with differences in the elimination maxima of 7, 31, and 38 degrees. By varying the weight ratio of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone, the effect of this type of variation on the composite curves of the distillation could be studied.

Distillation of Equal Weight Ratios of Dyes in Binary Mixture. In determining the composite curves for the distillation of a binary mixture, the concentration of each dye in each fraction was determined and the yield of each dye expressed as a weight per cent of the total of both dyes in the feed mixture. By summation of the yields of the individual dyes, the overall yield of dye in each fraction was determined and the composite curve could then be plotted. Tables XIII, XIV, and XV, pages 188, 192, and 194, give the data and results for the distillation of binary mixtures of equal weights of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone, celanthrene red 3B and 2,6-dimethyldiaminoanthraquinone, and 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone, respectively. The composite curves are shown in Figures 26, 28, and 29, pages 190, 193, and 195.

The distillation of the binary mixtures of dyes in equal weight ratios indicates that each dye distills independently of the other dye. By doubling the yield of any individual dye and comparing this figure with the yield of the dye when distilled singly for any one fraction, this fact can be established. For instance, if the 120-degree fraction be chosen for a study of celanthrene red 3B, it can be found in Table XIII, page 188, (for the distillation of a binary mixture of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone) that 13.7 weight per cent of the total dye feed was the yield for celanthrene red 3B. Since celanthrene red made up 50 weight per cent of the total dye, it follows that twice 13.7 per cent or 27.4 per cent of the total celanthrene red 3B was distilled in the 120-degree fraction. This last figure can then be compared with the yield of the 120-degree fraction when celanthrene red 3B was distilled alone which was 26.8 weight per cent for Test 1 and 27.4 weight per cent for Test 2 as shown in Table XII, page 184.

In a similar manner, other comparisons can be made which substantiate the statement that each dye distills independently of the other dye in a mixture. Perhaps a comparison of the yields at the maximum as determined from the elimination curves, rather than for any one or more fractions, would better establish this contention. Doubling each yield at the maximum for a single dye in a binary 1:1 weight ratio mixture and comparing with the maximum yield for the distillation of single dyes gives 30.5 compared with 29.0 weight per cent for celanthrene red 3B and 27.0 compared to 26.5 weight per cent for 1,4-diethyldiaminoanthraquinone from the distillation of the binary mixture of these two dyes. Similarly, for the other two 1:1 binary mixtures studied: 26.0 compared to 29.0 and 26.5 compared to 27.0 weight per cent for celanthrene red 3B and 2,6-dimethyldiaminoanthraquinone; 27.0 compared to 26.5 and 27.0 compared to 27.0 weight per cent for 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone.

The composite curves for the two substances with elimination maxima at varying intervals are interesting. In both the distillation of a 1:1 mixture of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone and of a 1:1 mixture of celanthrene red 3B and 2,6-dimethyldiaminoanthraquinone, the two elimination maxima of the individual dyes were relatively far apart, 31 and 38 degrees Centigrade, respectively. The composite curve for each of these two distillations (Figures 26 and 28, page 190 and 193) showed two maxima occurring at the same temperatures as the individual maxima of the two dyes in the mixture. It is evident, however, from just these two distillations, that the closer the two elimination maxima, the less distinguishable will be the maxima on the composite curve. Only the first maximum at 121 degrees Centigrade is pronounced for the distillation of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone while both are definite for the distillation of celanthrene red 3B and 2,6-dimethyldiaminoanthraquinone indicating the effect of a seven degree greater difference in the elimination. In the distillation of a mixture of 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone where there was a seven degree difference in the individual elimination maxima, the composite curve determined, Figure 29, page 195, had only one maximum, at approximately 159 degrees Centigrade with elimination maxima for the two dyes at 153.5 and 165 degrees Centigrade. The curve has an almost flattened top instead of the peaked top which had typified other maxima. This distillation served to give some indication of the difficulty encountered in analytical molecular distillation when substances with close elimination maxima are being studied.

This last test, the distillation of a 1:1 weight ratio of 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone, is interesting from another aspect. Since both dyes had relatively high elimination maxima compared to celanthrene red 3B, it was felt that the range of the constant-yield oil used in the test could be increased by using heavy mineral oil rather than a mixture of light and heavy mineral oils. Such was indeed the case as the first fraction was at 130 rather than at 100 degrees Centigrade and the last at 190 rather than 180 degrees Centigrade. The importance of the use of this heavy oil rather than the usual mixture employed in all the other tests is in the shift of the elimination maximum of 1,4-diethyldiaminoanthraquinone from 152 to 153.5 degrees Centigrade and the maximum of 2,6-dimethyldiaminoanthraquinone from 159 to 165 degrees Centigrade. Every condition of operation remained the same as in the other tests with the exception of the oil solvent used. The shift of the maxima was unexpected but explainable through a study of the effect of the use of only heavy mineral oil on the other variables. When light mineral oil was used in the solvent mixture, distillation began at 100 degrees Centigrade, and by the 130-degree fraction, over 150 milliliters of the original feed mixture of 650 milliliters had been distilled. Further, the 130-degree and 140-degree fractions yielded approximately 180 milliliters compared to 108 milliliters when only the heavy mineral oil was used. Thus, by the time the 150-degree fraction was being collected, there was over 500 milliliters left in the distilland when only heavy mineral oil was used compared to about 320 milliliters when the mixture of mineral oils was used. The smaller yields of mineral oil for the 130, 140, and 150-degree fractions and larger yields for the 160, 170, and 180-degree fractions than normal under standardized conditions could very easily have resulted in drainage error causing the elimination maxima to shift to a higher temperature for both dyes. This is further substantiated by the slight shift, 1.5 degrees, for 1,4-diethyldiaminoanthraquinone which has a maximum near 150 degrees Centigrade where the yield of constant-yield oil was about the same as when a mixture of oils was used, while the elimination maxima shifted somewhat more for 2,6-dimethyldiaminoanthraquinone, 6 degrees.

Distillation of Varying Weight Ratios of Dyes in Binary Mixture. Weight ratios of 2:1, 1:1, and 1:2-1/2 of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone were studied. The data and results for the distillations are given in Table XIII, page 188, and the composite curves, in Figures 25, 26, and 27, pages 189, 190, and 191.

It is of interest to note the varying shape of the composite curves as the relative amounts of each of the two dyes was changed. Each of the dyes again distilled independently of the other dye with elimination maxima of about 122 and 152 degrees Centigrade being obtained for celanthrene red 3B and 1,4-diethyldieminoanthraquinone, respectively, in all three tests. The composite curves, for these distillations, gave evidence that two substances were distilling in that two more or less definite maxima occurred in the curves. In all three tests, these maxima in the composite curve, fell at the same temperatures, 122 and 152 degrees Centigrade, as the individual elimination maxima of the dyes. With the 30-degree temperature difference observed in the maxima, it was noted that the presence of a second substance is easily recognized when this second substance is of such quantity as to be 1/5 of the weight of the first substance (the case of a 1:2-1/2 weight ratio). This was the greatest difference in the ratios attempted. It can further be estimated that it will become increasingly difficult to detect a second substance in a mixture when it is in quantity less than 1/5 that of the first substance. The first substance might be assumed to have merely an "odd" tail in its elimination curve and not be contaminated with a second substance.

In the case of the anthraquinone dyes employed in these tests, analysis for each dye was possible and the composite curve was determined by summation of the individual yields of dyes. No method might be available for the analysis of each fraction for the distillation of a mixture of two oils in an unknown ratio. In this case, the volume, rather than the weight, yields for each fraction might be used to plot the composite curve for the distillation. A comparison of this curve with curves obtained from the distillation of known (and analyzable) mixtures of substances might allow a good estimation of the relative volumes of each oil in the mixture and even possibly identification of each oil from the maxima obtained on the composite curve. Curves such as these determined in this investigation are important therefore as analytical tools in further distillations of unknown mixtures.

Separation of Binary Mixtures of Dyes. Two methods of redistillation were attempted to study the possible separation of a binary mixture of dyes: "extractive" redistillation and conventional "repeated" redistillation. Celanthrene red 3B and 1,4-diethyldiaminoanthraquinone with elimination maxima varying by 31 ± 1 degrees Centigrade were used in the binary mixtures of dyes. It was felt that the large difference in the elimination maxima would still permit a satisfactory separatory distillation study since the methods of separation and the effective separation obtained through their use was important rather than a desire to purify two closely-distilling substances. The standardized technique was employed in all the separatory redistillations without regard to the feed volume undergoing distillation.

Extractive Molecular Redistillation. The term, extractive molecular redistillation, was applied to the redistillation of cumulative fractions from a primary distillation after the addition of an amount of mineral oil to bring the cumulative volumes up to about the original feed volume employed in the primary distillation. In the test made, for instance, the original feed mixture volume was 650 milliliters of constant-yield mixture with a 2:1 weight ratio of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone dispersed in the oil. The original feed mixture was distilled and nine fractions from 100 to 180 degrees Centigrade were obtained. The cumulative volumes of the 100, 110, 120, 130, and 140-degree fractions were 286 milliliters. Of this 260 milliliters were employed in the extractive redistillation. Since it was desired to purify the celanthrene red which distilled over largely in the lower fractions, 340 milliliters of heavy (and higher-distilling) mineral oil were added to the 260 milliliters of previously distilled cumulative volumes to obtain a feed mixture differing by only 50 milliliters from the original feed volume, 650 milliliters. This new feed mixture was then distilled as was the original feed mixture. The data and results for the original and extractive distillations are given in Table XVI, page 196, and the curves for the elimination of the dyes appear in Figures 30A and 30B, pages 197 and 198.

Of the original weight of celanthrene red 3B in the feed mixture, 0.0200 gram, 0.0142 gram distilled in the 100 to 140 degree Centigrade range compared to 0.00298 gram of the original weight of 1,4-diethyldiamincanthraquinone, 0.0100 gram. Or expressed slightly differently, 71.0 weight per cent of the original celanthrene red 3B and 29.8 weight per cent of the original 1,4-diethyldiaminoanthraquinone were distilled in the cumulative fractions up to 140 degrees Centigrade. The cumulative fractions used in the redistillation therefore contained a binary mixture of 82.6 per cent celanthrene red 3B and 17.4 per cent 1,4-diethyldiaminoanthraquinone by weight. As the cumulative volume for redistillation was slightly less than the original volume collected, 260 of 286 milliliters, as described previously, the weights of the dyes in the feed mixture were slightly less than 0.0142 gram of celanthrene red 3B and 0.00298 gram of 1,4-diethyldiaminoanthraquinone, but the necessary calculations were made to determine the actual weights of each dye in the mixture. The weight per cent of each dye was still 82.6 and 17.4 per cent, however.

When the extractive redistillation was performed, each dye in the mixture distilled with an elimination curve as when distilled alone. The 1,4-diethyldiaminoanthraquinone which had previously distilled at 140 degrees Centigrade or below did not come off completely at this temperature and below in the redistillation. Instead, the elimination of this dye was to a maximum at 152 degrees Centigrade, Figure 30B, page 198, with most of the dye distilling over at temperatures above 140 degrees Centigrade. Similarly, some of the celanthrene red 3B distilled above 140 degrees but the major portion distilled below this temperature as in the original distillation. The natural tendency under molecular distillation for any dye to "seek" its characteristic elimination maximum was evidenced. The shift of much of the 1,4-diethyldiaminoanthraquinone to higher distillation temperatures resulted in a higher concentration of celanthrene red 3B in the 100 to 140-degree fractions. From calculations with data from Table XVI, page 196, the change in concentration of celanthrene red 3B in each fraction can be determined. These are 98.8 compared to 92.5, 98.2 to 94.2, 97.6 to 91.1, 94.8 to 80.4 and 85.3 to 58.6 weight per cents for the redistillation compared to the original distillation for the 100, 110, 120, 130, and 140-degree fractions, respectively. The cumulative concentration of celanthrene red 3B through the 140-degree fraction was compared to that of the original distillation as described above as 94.8 weight per cent compared to 82.6 weight per cent.

In the same manner as this distillation, light mineral oil, distilling largely in the lower fractions, could have been added to the cumulative fractions from 150 to 180 degrees Centigrade to "extractively" distill or assist in the purification of 1,4-diethyldiaminoanthraquinone.

One important aspect must be kept in mind in the complete evaluation of such "extractive" redistillation. Such a technique would seem to have little practical value in the industrial separation of substances since it entails considerable dilution of the potent material with mineral oil. If such dilution were not objectionable, the method would be of value since it provides somewhat better separation than mere redistillation as will be discussed in the following section. Another and more obvious advantage is the elimination of the necessity of numerous distillations to provide a sufficient volume for the feed mixture for redistillation. This extractive distillation technique might prove especially applicable in the analytical distillation of unknown substances from mixtures if the technique could be standardized. The choice of the additional oil to be used with the cumulative fractions is of importance in regard to a standardized technique as a constant-yield feed mixture would be desirable in both the original distillation and the redistillation before precise analytical distillation could be performed.

Conventional Molecular Redistillation. To study the separation of a binary mixture by repeated redistillation, two redistillations were made on an original 1:1 weight ratio of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone. Two duplicate batches of this weight ratio were distilled by the standardized technique. The cumulative fractions for both distillations for temperatures of 100, 110, 120, 130, and 140 degrees Centigrade totaled 693 milliliters. Of this volume, 557 milliliters were taken as the feed for the first redistillation. This feed mixture was distilled again using the standardized technique. Fractions were obtained for temperatures from 100 to 150 degrees Centigrade with a residue of 77 milliliters. The cumulative 100, 110, 120, 130, and 140-degree fractions totaled 428 milliliters. Of this volume

380 milliliters was used as the feed batch for the second redistillation from which were obtained 100, 110, 120, 130, and 140-degree fractions and a residue of 49 milliliters. In both the redistillations, the feed volume could not be equal to that obtained from the cumulative volumes of the fractions since a small sample of each fraction was reserved for colorimeter analysis and some loss occurred in the transfer of the volumes from one container to another. In each case, however, a proportional volume of each fraction was used to insure that the feed mixture would be of the same dye concentration as the cumulative volumes obtained would have been if mixed without loss or reservation of analytical samples. The data and results of the original distillations and the two progressive redistillations are presented in Table XVII, page 199, and the elimination curves appear in Figures 31A, 31B, and 31C, pages 200, 201, and 202.

It is immediately noted that a major weakness in this type of redistillation at least from an analytical standpoint, is the decrease in the size of the feed volumes from one redistillation to the next. For a separation where 10 or more redistillations might be necessary, the original distillations might have to be several dozen in number to obtain sufficient cumulative volumes for each fraction to provide feed mixtures of approximately the same volume as the original feed mixtures. Further, numerous redistillations might have to be performed at each step in the analytical separation for the same purpose. The variation in the constancy of the yields is also noted. The constant-yield oil used was a mixture of two oils which in turn have numerous constituents which have their own elimination characteristics as do the anthraquinone dyes. The constant-yield oil prepared from this mixture may have given relatively constant yields for a standardized procedure for the original distillations as was the case in this investigation. However, when the lower-distilling fractions were redistilled, the constancy of the yields is affected. This did, in effect, change the conditions of distillation from those of the standardized technique for the initial feed volumes are much decreased (650 to 557 milliliters for the first redistillation to 380 milliliters for the second redistillation). Even if the volumes could be kept constant sufficiently by increasing the number of original distillations, the temperature range of distillation would still be shifted. A comparison of an original distillation with the first redistillation will suffice to indicate this fact. Although the feed volumes varied by only 93 milliliters, the range of distillation changed from 100 to 180 degrees for the original distillation to 100 to 150 degrees for the redistillation. Significantly, the volumes of each fraction increased for the redistillation from fraction volumes obtained in the original distillation (35, 67, 107, 118, and 101 milliliters for the five fractions up to 140 degrees Centigrade compared to 19, 51, 83, 92, and 91 milliliters for these fractions from the second original distillation). The importance of these considerations is to indicate the possibility of varying amounts of drainage error in the redistillations as well as to note that little oil remains to "carry" the diethyl to its typical maximum. It would be expected that the shift (and subsequent separation from celanthrene red 3B) of 1,4-diethyldiaminoanthraquinone would not be as evident as in the extractive molecular redistillation. A study of the separation attained by these redistillations is in order.

The concentrations of celanthrene red 3B for the 100, 110, 120, 130, and 140-degree fractions were 96.6, 96.5, 94.3, 85.5, and 24.4 weight per cents for the first redistillation and 98.6, 97.6, 96.1, 91.4, and 64.5 weight per cents for the second redistillation compared to average concentrations for the original distillations of 93.3, 91.0, 86.2, 64.1, and 30.0 weight per cents for the same fractions, respectively. The increased concentration of celanthrene red is noted as was the case in the extractive redistillation.

Since the original feed mixtures were 1:1 weight ratios of celanthrene red 3B and 1,4-diethyldiamineanthraquinone rather than a 2:1 weight ratio as in the case of the extractive redistillation, a direct comparison of results for the two methods is impossible for an effective study of the separation obtained. The amount of 1,4-diethyldiamineanthraquinone removed from the total volume up to 140 degrees Centigrade as compared to that amount originally in the 140-degree fraction and below would provide a valid method of comparison of the two techniques, however, as the per cent removal of dye would be under study rather than the concentrations of dye obtained.

For the extractive molecular redistillation, 75.3 weight per cent of the original 1,4-diethyldiamineanthraquinone was removed from the combined 100 to 140-degree fractions as compared to 68.7 weight per cent and 52.8 weight per cent for the first and second conventional redistillations, respectively. The loss of celanthrene red to the fractions and residue above 140 degrees Centigrade was 11.9 weight per cent for the extractive redistillation compared to 13.5 and 13.8 weight per cents for the first and second redistillations, respectively.

The composite elimination curves for the redistillations as for the extractive distillation, Figures 31A, 31B, and 31C, pages 200, 201, and 202, are of little value other than to indicate the use of such curves in the analytical distillation of unknown mixtures. It is noteworthy that the elimination maximum of celanthrene red 3B remained at 121 to 122 degrees Centigrade for all the redistillations and that the maximum for 1,4-diethyldiaminoanthraquinone in the extractive redistillation was 153 degrees Centigrade, differing by only one degree from the normal maximum for this dye, 152 degrees Centigrade. No maximum was obtained for 1,4-diethyldiaminoanthraquinone from the conventional redistillations but the shape of the "tail" of the elimination curves for this dye seem to indicate that a normal elimination maximum would have been reached if distillation could have been continued (if higher-distilling mineral oil had been available for carrier oil).

Molecular Distillation of a Tertiary Mixture of Dyes. One distillation was carried out for a mixture of equal weights of the three dyes previously used in binary mixtures to obtain the composite curve, Figure 32, page 204. Two maxima are noted in the composite curve at temperatures of 121 and 154 degrees Centigrade again giving some indication of the increased difficulty of detecting the presence of closely-distilling substances.

Constructional and Operational Features of the Molecular Still and Still Accessories. Some of the constructional and operational features of the equipment used in this investigation will be considered to indicate points of particular interest or further need for modification of design.

Feed Pump. The importance of a vacuum-tight feed pump was emphasized when a Hills-McCanna proportioning pump failed to pump the feed to the rotor or permit the system to be properly evacuated because of improper seal of the piston of the pump. The copper, magnetically-operated pump employed in all the tests was most easily made vacuum-tight. The operation of this pump was not as satisfactory as desirable, however. At various times, often in the middle of a test, the plunger became stuck in the copper body of the pump and pumping ceased. In these cases, it was generally necessary to disassemble the feed pump to unloosen the plunger. This was facilitated by the soft-soldered body which allowed the pump to be disassembled and reassembled readily and which still served to make the pump vacuum-tight. The test being performed when the pump misfunctioned necessarily had to be restarted as spillage of part of the feed occurred on disassembly of the pump.

The control of the feed rate was generally not as satisfactory as desirable. If the feed rate changed during a test, the field coil had to be moved up or down relative to the pump body to change the length of the stroke of the plunger and thereby change the feed rate. Powerstat control of the feed pump was not found to be satisfactory in changing the feed rate by more than 10 milliliters per minute and was used for only minor adjustments. Two or more trial shiftings of the field coil were often necessary to correct the feed rate to the one desired, and individual determinations of each trial feed rate had to be made. Luckily, the feed rate often did not change for at least four or five temperature fractions (several tests were made without any change required in the pump setting) and this procedure was not necessary in these cases.

Rotor Bearing and Housing and Vacuum Enclosed Drive. The numerous unsuccessful attempts made to secure a vacuum-tight seal of the rotor drive shaft through the use of various packings and lubricants in the rotor housing are of interest. Often, when a new assembly was first tested, the vacuum obtained was adequate (below 10 microns and generally 2 to 3 microns of mercury, absolute) for several tests. But after some operation, leakage developed which could only be traced to the rotor housing. It was believed that the packing would hold the required vacuum when it was once broken in. This did not prove to be the case, however, as many hours of operation of the rotor to test this theory indicated. When an increased length of packed housing and the use of single and dual lantern rings for lubrication also proved unsuccessful, it was decided to enclose the drive motor in a vacuum chamber. The vacuum which could be attained with this arrangement, 6 microns of mercury, absolute, was not as good as had sometimes been obtained with the packed rotor housing for short periods, 2 microns, but remained essentially constant. Since this vacuum was constant and still permitted molecular distillation to take place, it was believed to be satisfactory and all tests using the standardized technique were made at this vacuum.

Vacuum Pumping System. That a vacuum lower than six microns could not be obtained was probably due to the fact that the system was not completely vacuum-tight. There are numerous other considerations to be made, however, before such a statement can be made conclusively. Many of the vacuum flow lines were 1/4-inch or less with many bends occurring in the system. Such an arrangement would limit the speed of evacuation of the system and result in a greater absolute pressure for very minor leaks than would have been the case if larger vacuum flow lines had been used. Further, both of the diffusion pumps were used in a series, the vacuum side of the second pump attached to the exhaust side of the first pump. It is entirely possible, and appears quite likely to this investigator, that a lower pressure would have been obtained from a connection of the diffusion pumps in parallel as were the megavac pumps attached in the system to the exhaust of the second diffusion pump.

McLeod Gage. The modified McLeod gage used throughout the tests to measure the absolute pressure in the system functioned satisfactorily despite the presence of a very slight amount of oil in the mercury reservoir of the gage. At intervals during the progress of the investigation, the gage mercury reservoir and the mercury were cleaned to remove the oil which had backed into the gage as oil vapor during the distillation tests since the previous cleaning. The only apparent effect of the oil in the mercury was in the need for extra precaution when taking readings to prevent a drop of oil from sticking in the capillary section of the gage which would later result in drops of mercury sticking in the capillary with poor readings being obtained until the mercury drop could be tapped loose and returned to the mercury reservoir. If a slight amount of oil merely remained on the surface of the mercury in the reservoir, no difficulties were encountered in the operation of the McLeod gage.

Heaters. Both the flexible sheath heater and the coil heater employed after the flexible sheath heater burned out were satisfactory for heating the feed through the temperature range studied in this investigation. The coil heater wrapped around, and thus was in more intimate contact with, the feed line and gave somewhat better control of the feed temperature than did the sheath heater. Further, this heater was used for a much longer period of time than was the sheath heater and did not burn out as did the sheath heater after approximately 75 hours of operation.

The ring-type heating element used to supply heat to the rotor also performed satisfactorily for the temperature range desired. It was necessary to control the amount of heat to the rotor very carefully as the large bulk of metal in the rotor retained heat for some time and was very slow to heat or cool.

It is estimated that distillation temperatures above 210 degrees Centigrade would have been impossible to obtain with the heaters now part of the assembly. At temperatures above 180 degrees Centigrade, much difficulty was encountered in keeping the temperature of distillation constant. No insulation was employed on the feed preheater line which might increase the temperature range of this heater somewhat. It was believed that insulation used with the sheath heater had been partly the cause of the heater burning out.

Thermocouple Construction and Calibration. The construction of the thermocouples used to determine the feed and residue temperatures is of particular interest. Part of the copper lead of the copper-constantan thermocouple was 1/8-inch copper tubing. The constantan wire was passed through the copper tubing and the hot junction formed at one end of the tubing by peening the tubing closed over the constantan wire and welding a junction of the wire and tubing. Copper wire was then soldered to the copper tubing at the other end of the tubing to form the copper lead. The copper tubing was in turn soldered within a short piece of 1/4-inch tubing which could be fitted with a compression type fitting. This construction allowed the insertion of the thermocouple into the feed line or through the base plate into the bell jar. This setup performed satisfactorily throughout the tests made, and gave surprisingly good sensitivity.

A comparison of the potentiometer readings with those given for definite temperatures for a standard copper-constantan thermocouple is of interest also. For temperatures of 100, 150, and 200 degrees Centigrade, readings for the feed thermocouples of 4.20, 6.64, and 9.09 millivolts; and for the residue thermocouple, 4.14, 6.36, and 8.58 millivolts; were obtained. These compare with standard readings for these temperatures of 4.28, 6.70, and 9.29 millivolts(61).

Colorimeter and Colorimeter Operation. The colorimeter afforded an accurate and rapid means of dye analysis for the various distillation fraction when used with the appropriate colorimeter calibration curves. One necessary precaution which had to be followed throughout all the analytical work was the proper "warm up" of the colorimeter before use. The time required for a "warm up" period varied with the three filters with 20, 30, and 60 minutes required for the blue, green, and red filters, respectively. Without this "warm up" period, the colorimeter pointer tended to drift and gave readings which were too high. No drifting of the pointer was observed when the proper "warm up" periods were observed.

Recommendations

The following recommendations are made for future studies and for modification of the equipment of the centrifugal molecular still for improved operation.

Recommendations for Future Studies. Several additional tests and studies are recommended for future work to enlarge the scope of research using the centrifugal molecular still.

Wider Range Constant-Yield Oil. In order to increase the number of substances that could be studied using the molecular still, the temperature range of the constant-yield oil would have to be increased. Under the conditions of distillation employed in this study, a mixture of light and heavy mineral oils provided a constant-yield oil that had a temperature range from 100 to 190 degrees Centigrade. The need is for an oil with a range from about 70 to 250 degrees Centigrade. Further, the amount of carrier oil which did not distill in the temperature range used in this investigation was less than 1/6 the original feed volume (approximately 100 milliliters of a feed volume of 650 milliliters) when an oil with 1/2 its original volume nondistillable would be more preferable.

To permit the use of the colorimeter, it would be necessary to obtain a colorless or nearly colorless oil or, at least, one which did not vary in color from fraction to fraction. It is not believed likely that a colorless oil covering the desired temperature range will be found. Studies should be made to determine the distilling temperature ranges of various petroleum and vegetable oils, however. It may be possible that a nearly colorless constant-yield oil might be obtainable by blending colorless fractions which distill from colored oils such as petroleum residues. It might also be possible that a constant-yield oil may be found that is nearly colorless in its distilling range although it has a large volume of dark nondistillables which would serve as carrier oil.

If analysis for the potent substance is possible by other than colorimetric means, the use of a colorless oil is not warranted and a constant-yield oil with an increased temperature range could probably be obtained from the distillation of various motor and other petroleum oils.

Number of Passes. It is recommended that the system be so modified that the number of passes of the feed over the rotor for each fraction could be limited to one pass. It is further recommended that the residue not be continually recycled as was the case in this investigation, but, instead, be collected during the distillation of each fraction in the residue tank and drained to the feed tank only after the complete collection of the fraction. The effect of recycling the feed and employing two nominal passes in this investigation was not studied. It is felt, however, that more exacting analytical distillation could be performed by a method which would insure the complete passage of all the feed over the evaporating surface.

This method could be studied with the equipment as it is at the time with no modification other than in the technique used. The time for a complete pass could be determined as was done in this investigation. Instead of allowing the residue to recycle to the feed tank, it could be collected in the residue tank. When the feed to the rotor stopped, the valve connecting the residue tank and the feed tank could be immediately opened to allow some residue to flow into the feed tank in order that the feed "holdup" in the feed line could be passed over the rotor to complete the one pass of the feed. The time for the volume of "holdup" to flow to the rotor would have to be calculated and distillation stopped when this time had been permitted after the opening of the residue drain valve. A great deal of care would be necessary to prevent overheating of the feed when the flow of feed ceased for a short time.

Distillate Fraction Temperature Increments. It is recommended that 5-degree temperature increments be used for fraction collection rather than 10-degree increments as used in this investigation. Smaller increments would allow more accurate determination of the elimination maxima. Further, the use of 5-degree increments rather than larger ones would slow the increase in the distillability as the distillability increases with temperature. This might permit more fractions to be collected than the 9 or 10 collected for the majority of tests made which, in turn, would increase the accuracy of plotting the elimination curves.

Separation of Mixtures. Much work need still be done to study the separation of mixtures by the various methods.

> Separation by Repeated Redistillation. Studies should be made to determine the best methods of repeated redistillation by which two or more substances of varying elimination maxima and in various weight or volume ratios could be separated. The number of redistillations to separate to an established degree two substances with elimination maxima differing by 5, 10, 20, and 30 degrees Centigrade could be studied to quantitatively evaluate the molecular still as a method of performing such distil-

lations. The anthraquinone dye series presents an adequate number of substances with the elimination maxima varying by such increments to permit a study of this type if the range of colorless constant-yield oil could possibly be increased to 250 degrees Centigrade.

Analytical Separation by Extractive Redistillation. It is recommended that further study be made on analytical separation of binary mixtures by the method of extractive redistillation employed in this investigation. To make such a method of analytical use would appear to require a wide study of constant-yield oils so that the "extracting" oil added to the cumulative fractions would make the feed mixture for redistillation as nearly a constant-yield oil as the original feed mixture. This would eliminate changes in the drainage error from the original distillation to any redistillation which might be made. A comparison of the extractive distillation technique with the repeated redistillation technique could be made with a binary mixture of two substances with elimination maxima varying by five degrees or less to ascertain which method is more advantageous for analytical separation.

Changing Feed Rate Instead of Distillation Time. Literature(62) reporting one method employed in operation of a falling-film still suggests a study which might be made in further attempts to determine the best technique available for still operation. Instead of shortening the time allowed for the feed to pass over the rotor for each fraction as the feed volume decreases during distillation, it is suggested that the feed rate be decreased so that the distillation time remains the same. This appears to be the method employed by most experimenters using the falling-film still in the laboratory and it should be interesting to note the difference between such a technique and the one employed in the investigation.

Isomer Study. An elimination maximum of 154 degrees Centigrade for 2,6-dimethyldiaminoanthraquinone rather than 141 degrees Centigrade which can be predicted for 1,4-dimethyldiaminoanthraquinone from the study of other members of the same series indicates the possibility that relatively wide intervals may occur between the elimination maxima of many other such isomers due merely to the sidechains or structure of the molecule. A future study of these two forms of the dye as well as all other available isomers of dimethyldiaminoanthraquinone is recommended to definitely establish the importance of the molecular structure on the elimination maximum of pure isomers of a substance.

The possibility of a difference in the elimination of isomers presents an interesting and potentially valuable study. If it can be established that certain isomers do differ in elimination maxima, then separation of these isomers by use of the molecular still would probably be possible. Isomers of the fatty acids and other substances could be studied as well as the anthraquinone dyes.

Recommendations for Modifications of System. The following recommendations for modifications to the equipment are made to improve operation of the molecular still.

Fractionating Barrier. In an attempt to improve the separating ability of the molecular still, a fractionating barrier of either a fine mesh screen or cooling coils could be placed directly in front of the rotor to partially condense some of the vapor leaving the rotor. A gutter would have to be placed directly below the fractionating barrier to permit separate drainage of the distillate which condensed on the barrier. The use of cooling coils would permit the investigator to obtain various amounts of partial condensation by varying the temperature of the water flowing through the coils.

Heaters. The feed preheater and rotor heater elements on the still at the present time will not permit the distillation of substances at temperatures above 200 degrees Centigrade. The system could be insulated to increase the temperature range of the heaters and this would probably make the feed preheater satisfactory. However, it is recommended that the 300-watt rotor heater be replaced with a 660-watt, type A-65 heater which can be purchased from the E. L. Wiegand Company, Pittsburgh, Pennsylvania.

Vacuum Pump Arrangement. It is recommended that the diffusion pumps be connected in parallel rather than in series. Further, it is recommended that a third megavac pump be connected in parallel with the other two megavacs now being used to exhaust the two diffusion pumps. It is also suggested that a megavac pump, rather than the smaller hyvac pump now being used, be employed to evacuate the distillate tank in order that this tank may be more rapidly evacuated and to achieve lower pressure in the tank so that the over-all system will not be affected when the distillate is being collected.

Enclosed Feed Pump. The copper, magnetically-operated feed pump was often difficult to regulate and gave pulsating feed resulting in a non-uniform layer of feed on the rotor.

Feed rates lower than 50 milliliters per minute and over 100 milliliters per minute were difficult to obtain and even more difficult to maintain constant. The need is for a pump which will provide a uniform flow and still not result in loss of vacuum. It is recommended that a small gear pump and variable speed motor for the drive be enclosed in a vacuum chamber similar to the one enclosing the rotor drive in this investigation. The vacuum chamber could be evacuated as part of the whole system or individually by the use of a separate megavac pump. A powerstat could be used to regulate the variable speed motor and thus the feed rate as desired.

Larger Flow Lines. It is recommended that the vacuum flow lines be increased to as large as practical to permit more rapid evacuation of the system and possibly lower pressure of operation. The vacuum outlet from the vacuum chamber to the diffusion pumps should be increased from 1-inch copper pipe to at least 2-inch copper pipe. Further, all 1/4-inch and 5/16-inch lines for vacuum flow should be increased to at least 1/2-inch copper tubing. Fittings on all vacuum lines should be of the Swagelok type or the connections should be silver-soldered. Special vacuum valves should be used to replace the valves now on the system where practicable.

Limitations

A centrifugal molecular still with a five-inch rotor and bell-jar condensing surface was used to study the molecular distillation of individual and mixed anthraquinone pilot dyes. The limitations imposed on this investigation include those of dyes used, pressures, rotor speed, feed rate, nominal number of passes, feed and residue temperatures, mineral constant-yield oil and analysis of samples from distillation.

Dyes Used. The anthraquinone dyes used in this study were celanthrene red 3B, 2,6-dimethyldiaminoanthraquinone, 1,4-diethyldiaminoanthraquinone, 1,4-diisopropyldiaminoanthraquinone, and 1,4-dibutyldiaminoanthraquinone. The first three of these dyes were used in the distillation of binary and tertiary mixtures of dyes. Celanthrene red 3B and 1,4-diethyldiaminoanthraquinone were used in the separatory attempts. The quantities of each dye used in any one test varied from 0.0071 gram to approximately 0.0450 gram.

Pressure. The tests were conducted at pressures varying from 1 to 7 microns of mercury, absolute. The first distillations used in establishing a standardized method of procedure were made at 2 ± 1 microns. Single elimination curves for the three dyes and those for binary and tertiary mixtures were obtained from distillations made at 6 ± 1 microns. At this latter pressure, the gap between the rotor and the bell jar was approximately twice the mean free path of the gaseous molecules.

Rotor Speed. Although the rotor speed was found to have no effect on the distillation, a rotor speed of 2000 ± 50 revolutions per minute was used on all the tests except for the first six distillations comparing the continuous and discontinuous techniques for which a rotor speed of 1720 ± 5 revolutions per minute was used.

Nominal Number of Passes. The number of passes of the feed over the rotor was not limited to a definite number for the three tests employing the continuous technique but can be estimated as being from 7 to 50 passes for the 100-degree fraction to the 180-degree fraction, respectively. Five nominal passes were employed for the three discontinuous temperature rise technique tests. The standardized method of procedure employed two nominal passes and the study of the distillation of binary and tertiary mixtures was made using this number of passes.

Feed and Residue Temperatures. The temperature differential between the feed and the residue was held constant at 10 degrees to within 1/2 degree for all tests. This temperature difference was chosen since it was relatively easy to maintain and did not result in flashing of the distilland because of overheating.

Mineral Constant-Yield Oil. The mineral oil solvent employed in the tests was a mixture of light and heavy mineral oils made up in a volume ratio of 8 parts of heavy oil to 7 parts of light oil. In one exception, the distillation of a binary mixture of 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone, only heavy mineral oil was used as the dye solvent.

Analysis of Samples. All analytical work on dye fractions was done with a Klett-Summerson colorimeter and used colorimeter calibration curves for the various dyes prepared by making and analyzing known concentrations of dye solutions in light mineral oil.

V. CONCLUSIONS

The molecular distillation of several anthraquinone dyes was studied using a laboratory centrifugal molecular still with a five-inch rotor and a bell-jar condensing surface. A standardized technique of operation was followed and the operating conditions were maintained constant as follows: pressure, 6 ± 1 microns of mercury, absolute; rotor speed, 2000 ± 50 revolutions per minute; feed rate, 65 ± 2 milliliters per minute; nominal number of passes of the feed across the rotor for each fraction, 2; and difference between the feed and residue temperatures, 10 degrees Centigrade. From the investigation, the following conclusions may be drawn:

1. Each dye in a mixture of two or more dyes distills independently of the other dyes in the mixture. The elimination maxima of celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone were 121, 152, and 159 degrees Centigrade whether distilled separately or in binary or tertiary mixtures.

2. The introduction of each two CH_2 groups in the 1,4 position of the anthraquinone dye series increases the elimination maximum by approximately 10 degrees Centigrade. The difference in the elimination maxima of three consecutive members of this

series, 1,4-diethyldiaminoanthraquinone, 1,4-diisopropyldiaminoanthraquinone, and 1,4-dibutyldiaminoanthraquinone, was 10 and 11 degrees, respectively.

3. The presence of a second substance in an unknown mixture can be detected if the second substance is in quantity at least 1/5 that of the first substance and has an elimination maximum differing by at least 20 degrees Centigrade from the elimination maximum of the first substance.

4. With differences in the elimination maxima greater than 30 degrees Centigrade, the composite curves for binary mixtures exhibit maxima at the same temperature as the individual maxima of the dyes. The distillation of an equal weight binary mixture of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone with elimination maxima varying by 31 degrees Centigrade gave a composite curve with maxima at 121 and 152 degrees Centigrade, the same maxima as for the individual dyes.

5. Extractive molecular redistillation results in better analytical separation of binary mixtures of dyes than does repeated redistillation. The amount of 1,4-diethyldiaminoanthraquinone removed from celanthrene red 3B was 75.3 weight per cent of the original as compared to 68.7 weight per cent for the first redistillation and 52.8 weight per cent for the second redistillation.

VI. SUMMARY

Molecular distillation presents a method of separation for substances of high molecular weights which would suffer thermal decomposition at the higher temperatures that would be required for conventional distillation. In general, the separatory power of molecular stills is poor and in order to obtain relatively pure substances from mixtures, a series of redistillations may have to be performed.

The distillation of individual substances under molecular distillation conditions is best characterized by an elimination curve which is a plot of the yield of the substance against the temperature of distillation. Composite curves, similarly, describe the elimination of a mixture of substances.

It was the purpose of this investigation to study the distillation characteristics of several anthraquinone dyes by the determination of single and composite elimination curves, and to attempt to separate binary mixtures of dyes by various redistillation techniques.

The glass centrifugal molecular still with a five-inch rotor and a bell-jar condensing surface available at the beginning of the investigation was almost completely reconstructed as an all-metal unit employing copper and brass as the materials of construction. Final design included a vacuum-enclosed drive for the rotor. Other modifications included a copper, magnetically-operated feed pump; copper tubing flow lines with silver-soldered connections; copper feed, residue, and distillate reservoir tanks; spark plug leads for heater and motor lead attachments within the vacuum system; feed and residue thermocouples employing copper tubing as part of the copper lead of the copper-constantan hot junction; a silicone gasket for seal of the bell jar to the base plate; a copper feed tube and nozzle; and a vacuum pumping system consisting of two vertical diffusion pumps connected in series and exhausted to two megavac pumps and a hyvac pump to evacuate the distillate tank.

Initial tests were made to obtain a constant-yield oil and to standardize an operating technique. A mixture of light and heavy mineral oils was found to be a satisfactory constant-yield oil. Several tests were made using a continuous temperature rise technique in which the distillate fractions were collected as the temperature rose slowly over the collection increment. 1,4-Diethyldiamineanthraquinone, 1,4-diisopropyldiamineanthraquinone, and 1,4-dibutyldiaminoanthraquinone dyes were distilled using this method. A discontinuous temperature rise technique replaced the continuous technique when it became evident that this initial technique could not be satisfactorily standardized. Instead of a continuous temperature increase as distillation progressed, the temperature was held constant while fractions were collected for a predetermined time interval required for five nominal passes of the feed across the rotor.

A standardised technique was then developed and used for all subsequent tests. The conditions of operation under this technique were as follows: pressure, 6 ± 1 microns of mercury,,absolute; rotor speed, 2000 ± 50 revolutions per minute; feed rate, 65 ± 2 milliliters per minute; nominal number of passes of the feed across the rotor for each fraction, 2; and difference between the feed and residue temperatures, 10 degrees Centigrade. The oil solvent, constant-yield oil, was a mixture of 300 milliliters of light mineral oil to 350 milliliters of heavy mineral oil for each test.

Three anthraquinone dyes, celanthrene red 3B, 1,4-diethyldiaminoanthraquinone, and 2,6-dimethyldiaminoanthraquinone, were distilled individually using the standardised technique. The elimination curves were plotted and the maxima found to be 121, 152, and 159 degrees Centigrade, respectively. Equal weight binary mixtures of celanthrene red 3B and 1,4-diethyldiaminoanthraquinone, celanthrene red 3B and 2,6-dimethyldiaminoanthraquinone, and 1,4-diethyldiaminoanthraquinone and 2,6-dimethyldiaminoanthraquinone were distilled to study the effect of difference in the temperature interval between elimination maxima on the composite curve. The effect of varying the weight ratio was studied by the distillation of binary mixtures of 2:1, 1:1, and 1:2-1/2 weight ratio of celanthrene red 3B to 1,4-diethyldiaminoanthraquinone. A tertiary mixture of equal weights of the three dyes used in binary mixtures was distilled to note the added complexity of the composite curve. Attempts to separate binary mixtures were made by extractive redistillation in which additional mineral oil was mixed with the cumulative fractions from the original distillation before redistillation and repeated redistillation in which the cumulative fractions were merely redistilled without addition of any more oil.

It was concluded from the investigation that each dye in a mixture distills independently of the other dyes present. The introduction of each two CH_2 groups in the 1,4 position of the anthraquinone series was found to increase the elimination maximum by approximately 10 degrees Centigrade. From a study of the composite curves for the various binary mixtures, it was decided that identification of two substances in an unknown mixture was possible if the second substance was in quantity at least 1/5 that of the first substance and had an elimination maximum at least 20 degrees Centigrade different from the first substance.

A comparison of the weight per cent of 1,4-diethyldiaminoanthraquinone removed from the mixture with celanthrene red 3B by the two redistillative techniques indicated that extractive redistillation provided better separation than repeated redistillation with 75.3 weight per cent removed from the cumulative fractions up to 140 degrees Centigrade compared to 68.7 and 52.8 weight per cents removed by the first and second redistillations, respectively.

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