USE OF A NON-INFLAMMABLE SOLVENT MIXTURE FOR THE EXTRACTION OF TUNG OIL

by

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TABLE OF CONTENTS

TABLE OF CURVES

TABLE OF FIGURES

I. INTRODUCTION

Tung oil, also known as chinawood oil or Chinese wood oil, is the product of a tree of the Aleurites genus which originated in China. The oil is found in its natural state in the cell of the seeds. While at the present time tung oil is expressed by mechanical means, it may be feasible for solvent extraction to replace mechanical expression.

In the United States, which is the outstanding consumer of tung oil, many industries are dependent upon tung oil as an essential raw material. More than eighty per cent of the tung oil consumed in American industries is utilized by paint and varnish manufacturers. The second largest consumer of tung oil is the linoleum industry. Considerable quantities of tung oil are also essential in the manufacture of certain insulating compounds for the electrical industry. Minor uses of tung oil are in some automobile brake linings; in the gaskets in steam pipes, pumps, and engines; in the table oilcloth industry; in waterproofing various types of fabric; and to some extent in the waterproofing of cartridge shells and for many other products requiring a waterproof coating.

Because of adulteration due to crude methods of expression, deliberate adulteration with inferior and less costly oils, lack of reliability of supply, and the opportunity for providing an economic use for certain waste lands and for providing

additional employment, the United States Department of Agriculture, for a number of years, has carried on extensive investigations in the planting of tung trees and the subsequent expression of oil from the fruit.

The climatic conditions for successful growth are exacting and successful plantings have been made only in northern Florida, the southern parts of Alabama, Louisiana, Georgia, and Mississippi, and the Gulf Coastal regions of Texas. The southern and northern limits of tung tree culture are determined principally by temperature considerations. The western limit of successful planting is considered at about 98° longitude in Texas(5) since experiments made in regions west of that line have shown that the rainfall was insufficient or too irregularly distributed throughout the year to provide proper nourishment.

Although the five million pounds of tung oil produced domestically in 1940 is hardly comparable to the ninety-seven million pounds of oil imported in 1940, rapidly increasing plantings of tung trees and studies by the Department of Agriculture point to a great increase in available tung nut crops in future years. Consequently the treatment of present and future crops so as to obtain maximum yields most economically is a problem of considerable importance.

The tendency in oil mill practice has been towards solvent extraction of many types of seeds because of the resulting economies. For example, in the case of linseed oil, only one per cent of the oil is left behind in the cake after solvent

extraction as compared to from eight to ten per cent remaining after mechanical expression.[32] Similarly solvent extraction of soybean oil produces a meal with six-tenths to one per cent residual fat as compared to a residual fat content of from four to five per cent for mechanically pressed meal.[4]

It appears feasible that tung oil may be solvent extracted by analogous methods thus decreasing the loss of oil in the cake and increasing the efficiency and economy of tung oil production in the United States. Consequently this study was undertaken in order to investigate the efficacy of various solvents and to obtain and correlate data in such form so as to be readily available for design calculations.

II. REVIEW OF LITERATURE

Tung Tree Culture in China. In China the tung trees occur "abundantly and grow luxuriantly mostly in a region between 26° and 34° North latitude and in hilly country up to 2,500 feet in altitude, especially in the upper reaches of the Yangtze valley. Aleurites fordii favors the northern and Aleurites montana the southern parts of the area, but there is no strongly marked division in the distribution of the species."(18) The montana species is less hardy than the fordii and is very sensitive to cold. The fordii species is by far the more important of the two. It accounts for more than ninety per cent of the total Chinese tung seed used in tung oil production. The oils of the two species are so nearly identical in character that the trade makes no distinction between them and they are commonly mixed and sold as tung oil.

Aleurites fordii as it flourishes in China has a rather short productive period, beginning to bear seeds three or four years after planting and continuing for a period of twelve to twenty or more years thereafter.(6) Aleurites montana are a year or two later coming into bearing, and do not bear as heavily but they are reported to live longer in China than Aleurites fordii.

Although China is the world's source of supply for tung oil, the production and marketing of the oil in that country

is carried on with relatively primitive and inefficient methods. The nuts grow wild, mature, and fall to the ground where they dry. They are later gathered, roasted, and crushed in crude mills scattered over the entire production area. The oil is then collected at various ports along the Yangtze river. Hankow is the most important collection center. The oil is then shipped down the Yangtze river in junks to Shanghai and from there to the different world ports.

Tung Tree Culture in the United States. Although tung trees had been planted as early as 1904, the first bearing grove of tung trees in America to furnish a crop sufficient to make possible the first expression of tung oil in the United States was planted in 1912. Subsequently the Florida State Department of Agriculture became interested and initiated work on tung nuts. The fordii species is the one which has been grown successfully in the United States although the Aleurites montana may someday prove to be valuable as a source of oil in central and southern Florida where the hardier species does not thrive.

"The areas for successful commercial growing of the trees in the United States are limited to a narrow strip fifty to one hundred miles wide in most places, along the Gulf Coast, the northern fourth of Florida, and the extreme southern and southeastern parts of Georgia. The Pacific coast and southwestern regions are excluded because of deficient rainfall and the cost of necessary irrigation. The more northern localities in the Southeastern States are of uncertain value because of

frequent injurious winter cold."(7)

Domestic commercial production of tung oil was started in 1932 when two full tanks of oil were shipped from Gainesville, Florida. Production figures in millions of pounds for the years following 1932 were as follows:(47)

(Frosts damaged crops in old years.)

1933 --- 0 1934 ---½ 1935 --- 0 1936 --- 2

1937 --- ½ 1938 ---3 1939 --- 3/4 1940 --- 5(27)

On April 1, 1940 there were nearly thirteen million tung trees in the United States, grown on 2,304 farms, of which 831 were in Mississippi, 373 in Louisiana, 367 in Florida, 283 in Georgia, 207 in Alabama, 204 in Texas, 29 in South Carolina, and 10 in California.(27)

At present the oil is obtained in the United States by mechanical expression. "The tung fruits fall from the trees in the late fall and are allowed to lie on the ground until they dry out sufficiently so that they can be safely stored without danger of heating. They are then collected and stored indoors in ventilated bins until they have dried sufficiently for hulling and pressing. The dried fruits are passed through a decorticator which removes the hulls and shells from the kernels, and then go to the shakers and separators where by mechanical and pneumatic action the kernels are separated from the hulls and most of the shells. The shelled kernels are ground and passed through the expeller or press (between a cylinder of steel bars and a center shaft of broken screw

construction) where the oil is pressed from the ground kernels. The pressed oil is passed through a filter to the storage tank."(44)

American tung oil is generally superior to that produced in China and has commanded a premium of from two to four cents a pound more than the Chinese product. The high specific gravity, high refractive index, low acidity, short time of polymerization with heat test, and excellent color of American tung oil are noteworthy.

Although American expressed oil has been shown to be far better than imported oil and has been obtained in greater yields due to the use of more modern equipment for expression, not all the oil is removed from the tung nut by mechanical expression. The cake which remains has an oil content of from four to ten per cent.(15) In 1940 when the domestic tung nut crop yielded five million pounds of oil, the oil discarded in the press cake was probably in excess of two hundred and fifty thousand pounds.(38)

Description of Tung Nut. The dry tung fruit has a smooth hull enclosing several nuts or seeds. The nut is made up of a shell, or pellicle, and a kernel. The shell is hard and brittle and is generally filled completely by the kernel or meat.

Composition of Tung Nut. "The seeds constitute slightly over half the weight of the matured fruit, the kernels about thirty, and the oil about twenty per cent. The oil content of the kernels ranges from about forty to fifty-eight per cent, depending upon their moisture content. Kernels from thoroughly

mature seeds usually contain about fifty per cent of oil."[20]

A typical set of results on part time operation of a commercial tung oil expression plant are:[44]

Meal --- 31 to 36 per cent of the fruit

Oil ---- 14.7 to 17.7 per cent of the fruit

Oil ---- 42.1 to 53.2 per cent of the meal

Oil ---- 310 to 390 pounds per ton dried fruits

Oil in cake --- 5 per cent

Composition of Tung Oil. A. Steger and J. Van Loon[41] reported the following percentages of constituents in a sample of Hankow tung oil: Unsaturated acids 86.4; saturated 4.9 consisting of 3.7 palmitic acid, and 1.2 of stearic acid; unsaponifiable matter 0.6; volatile matter 3.4; and glycerol as C_3H_2, 4.7. Van Loon later reported[45] that in the 86.4 per cent unsaturated acids, 72.8 per cent of the original sample was eleostearic acid and 13.6 per cent was oleic acid.

Eleostearic acid or oleomargaric acid as it was formerly called has been shown to be an unsaturated fatty acid of the empirical formula $C_{18}H_{30}O_2$ containing two double bonds in the molecule.[37] Several structures have been proposed for eleostearic acid.

Majima[29] suggested:

$$CH_3.(CH_2)_3.CH{:}CH.(CH_3)_2.CH{:}CH.(CH_2)_7.COOH$$

Fokin[14] suggested:

$$CH_3.(CH_2)_3.CH{:}CH.CH{:}CH.(CH_2)_9.COOH$$

According to Dean however, later work has shown eleostearic acid to consist of three double bonds:[8]

$$CH_3.(CH_2)_3.(CH:CH)_3.(CH_2)_7.COOH$$

Whitmore[46] proposes the structure of eleostearic acid to be the 9, 11, 13 - isomer of linolenic acid which is identical with the structure suggested by Dean. According to Whitmore, eleostearic acid, in the form of glycerides, constitutes more than ninety per cent of tung oil.

The principal component of tung oil, the glyceride of eleostearic acid, usually referred to as eleostearin exists in two forms, the ordinary liquid form called alpha-eleostearin and a solid, white, lard-like form known as beta-eleostearin. This solid form is different from tung oil which has either jelled by polymerization or has dried by oxidation. According to Freeman and McKinney,[16] solvent extraction favors the formation of the solid isomer, but the solid form so obtained can be made permanently liquid by heating the oil for thirty minutes at 250 degrees centigrade. Dean[9] reports this solid isomer formation to be due to exposure to light or to the presence of traces of iodine or sulfur.

Analysis of Tung Nuts and Tung Oil. Tung fruits may be analyzed for oil content by a method outlined by McKinney and Freeman.[31]

Acid number, saponification number, and other standard analytical constants may be determined by the methods outlined by Jamieson[21] and Gardner.[17]

History of Oil and Fat Extraction. Extraction of seeds by volatile solvents was first introduced in 1843 by Jesse Fisher[23] who manufactured carbon bisulfide on a commercial scale but did not patent his process. Thirteen years later E. Deiss patented the extraction of seeds by means of carbon bisulfide, and added "chloroform, ether, essences, benzine, and benzol to the list of solvents." This process made little progress for several years afterwards due mainly to the impure carbon bisulfide then manufactured which tainted both the oil and the extracted seeds.

In 1863 a patent was granted to Richardson, Lundy, and Irvine for extracting oil from crushed seeds or from refuse cake by the solvent action of volatile hydrocarbons from petroleum, earth oils, asphaltum oil, coal oil, or shale oil, such hydrocarbons being required to be volatile under 100 deg. C.

Since then, with the growth of the organic chemical industry, many additional solvents have been investigated and found to be miscible with fats and oils, some to be eliminated because of excessive costs, others to be eliminated because of high boiling points which might be injurious to certain fats and oils, others because of difficulty of recovery, etc.

Requisites of an Ideal Solvent. An ideal solvent would have the following characteristics:[33]

1. It should neither be inflammable nor explosive.

2. It should vaporize with the use of the minimum amount of heat.

3. It should dissolve only the oil from the meal of the seeds.

4. It should have good solvent properties.

5. It should distil within narrow limits of temperature, leaving no non-volatile residue.

6. It should have no toxic effect on the health of the workpeople.

7. It should not cause chemical change in the material under treatment.

8. It should have no deteriorating action on the works plant.

9. The cost must be low.

In addition there might be added availability and reliability of supply as requisites of an ideal solvent.

No solvent fulfills all these requirements; consequently in the selection of a suitable solvent, some of these requirements must be forsaken.

Solvents Applicable to Tung Oil. Morrell and Wood[33] list the following solvents as suitable for drying oil extraction: 1. carbon bisulfide 2. chloroform 3. carbon tetrachloride 4. benzene(comml.) 5. light petroleum 6. trichlorethylene and 7. turpentine.

According to McKinney[30] "most of the aliphatic and aromatic hydrocarbons, their halogenated products and the lower molecular weight ketones are miscible with tung oil." However, many of the solvents falling into these classifications

could be eliminated by application of the requirements of an ideal solvent.

Mixed Solvents. One of the most serious drawbacks to solvent extraction is the fire hazard due to the use of flammable solvents. Taylor[43] states that the Ford solvent extraction process for soybeans has been fairly safe in experienced hands, "but not until a suitable non-inflammable solvent can be found is it probable that the unit will be put on the market for individual farmer or community use."

Of the solvents listed by Morrell and Wood as being suitable for oil extraction, only three (chloroform, carbon tetrachloride, and trichlorethylene) are non-inflammable. However, these chlorinated compounds are much more expensive than the other solvents.

It is possible that less costly but flammable solvents can be mixed with more costly but non-inflammable solvents so that the resulting mixtures will be non-inflammable and will not give rise to flammable mixtures upon distillation. If the cheap flammable solvents can be mixed in sufficient proportions to reduce considerably the quantity of expensive non-inflammable solvents required and not diminish the oil extracting powers of the solvents, the fire hazard can be reduced more practically than if the more expensive non-inflammable solvent were used alone.

Sievers and McIntyre[40] experimenting with gasoline, benzene, carbon tetrachloride, and trichlorethylene found

that non-inflammable mixtures could be obtained which would fractionate safely and would effect a considerable saving over the use of the pure non-inflammable solvents.

The method of testing consisted of introducing 2 cc. of the solvent mixture under investigation into a 300 cc. beaker which was kept sufficiently hot by a hot plate to vaporize the solvent immediately. In the midst of the vapors, a spark plug suspended in the beaker was discharged at frequent intervals. Those mixtures which did not burst into flame from the spark were considered sufficiently non-inflammable for use in an extraction plant.

A mixture consisting of 70 per cent carbon tetrachloride and 30 per cent benzene by volume was found to be safe. However, these percentages are not absolute since mixtures were made up only for five per cent intervals.

To test the safety of fractionating such a mixture, Sievers and McIntyre distilled by direct heat 500 cc. of a 70 per cent carbon tetrachloride - 30 per cent benzene mixture by volume and collected ten - 50 cc. portions. All fractions were found to be safe.

Steam distillation of 500 cc. of a mixture of the same composition yielded ten fractions the last of which was of doubtful safety. Therefore Sievers and McIntyre suggested that the original mixture should contain at least 72 per cent by volume of carbon tetrachloride in order to be safe for steam distillation.

Water is slightly soluble in carbon tetrachloride and benzene and no mention is made in the article of water being removed from the ten fractions that were steam distilled. It is possible that the carbon tetrachloride - benzene mixtures dissolved some water during the steam distillation thereby decreasing the densities of the resulting fractions. Decreased densities would indicate higher benzene contents since the compositions of the resulting solutions were determined solely by density measurements. This may account in part for the "unsafe fraction" that was obtained upon steam distillation.

Dodge[12] criticized Sievers and McIntyre's method of obtaining the data on the basis that from the nature of the test outlined, "the concentration of the solvent vapors must have been indefinite and consequently the possibility of ignition is determined not only by the relative amounts of, say, benzene and carbon tetrachloride, but also by the concentration of oxygen." Dodge concluded by stating that one is not justified in drawing any conclusions concerning the effect of carbon tetrachloride upon benzene and gasoline from the tests conducted by Sievers and McIntyre.

However, the results obtained by these two investigators are in agreement with the results obtained in this investigation and with the compositions suggested by Underwriters' Laboratories, Inc.[28] and the Pennsylvania Salt Manufacturing Company[42] who recommended a 70 per cent carbon tetrachloride-30 per cent benzene mixture by volume for an initial non-inflammable safe mixture, this composition being on the safe side.

Steps in the Solvent Extraction of Tung Nuts. The steps required in the solvent extraction of tung nuts would be:

1. Shelling the nuts.
2. Proper grinding of the kernels.
3. Percolation of the solvent through the ground kernels.
4. Distillation of the solvent from the oil and subsequent condensation of the solvent.
5. Removal of the solvent remaining in the cake.

Expressions Used in Solvent Extraction. Expressions used in solvent extraction are defined by Sherwood[39] and Perry.[35]

Based upon their two definitions, solvent extraction may be defined as the separation of the components of a liquid or solid mixture by treatment with a second liquid in which one or more of the components of the mixture are soluble. The solvent layer which forms is termed "extract" and the treated solution "raffinate".

Solvent extraction may further be divided into liquid-liquid extraction which is the treatment of a liquid solution with an immiscible solvent and leaching which includes the extraction operations involving the separation of a solid mixture or phase into its components by treatment with a liquid.

The special case of leaching with which this investigation is concerned involves the transfer of the soluble constituent (tung oil) from the insoluble one (tung kernels) into the solvent by diffusion through a membrane.

Solvent extraction is a broader term embracing the expression leaching, and in the discussion to follow, solvent extraction, extraction, and leaching will be used interchangeably to avoid repetition with the understanding that these terms refer to the transfer of tung oil from tung kernels into a solvent by diffusion.

Solvent Extraction Methods. The simplest type of operation is the single contact, in which the solvent and the original mixture are brought together for a single batch extraction. The amount of solute extracted per unit amount of original mixture is determined by the amount of solvent used, the distribution relations for the system involved, and the extent to which equilibrium is approached. The equipment used for a single contact extraction is shown diagrammatically in Figure 1. (It is possible to perform the mixing and separating in one piece of equipment.) The efficiency of this operation is definitely limited and consequently single batch extraction is seldom employed for large-scale work.

An improvement over the single contact type of leaching is obtained by extracting the solid with solvent, removing the extract, and then extracting the solid again with fresh solvent. The reduction of solute content of the raffinate may be improved to any desired extent by increasing the number of contacts. In the simple case where the distribution law holds, the maximum efficiency is obtained when the total solvent is divided into equal parts, the same

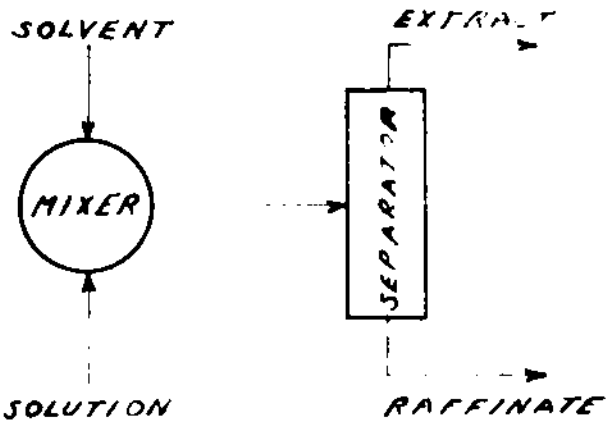


FIGURE 1

SINGLE CONTACT EXTRACTION

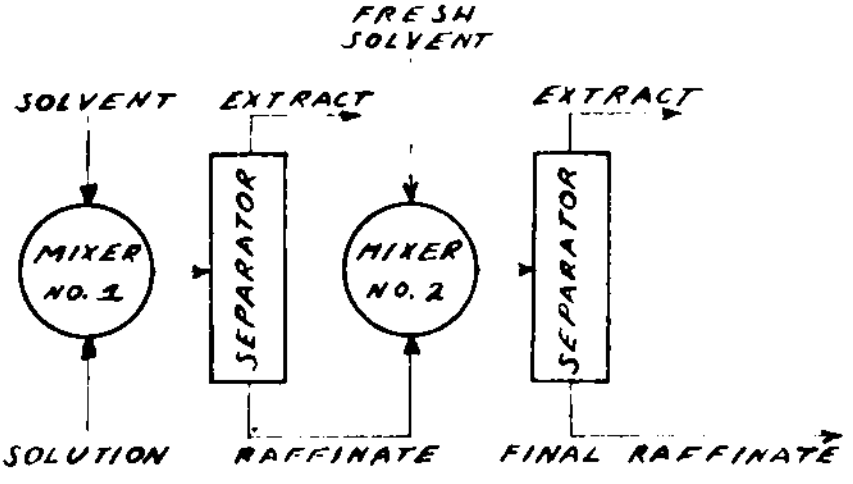


FIGURE 2

MULTIPLE CONTACT EXTRACTION

quantity being employed in each stage. The equipment necessary for this multiple contact type of extraction is shown in Figure 2.

A further improvement is illustrated in Figure 3 where the solvent properties of the weaker extracts are utilized by passing the material to be extracted and the solvent through the system in opposite directions. The illustrated system involves three stages, although any number may be used. All the solvent passes through each stage and the over-all efficiency, for a given amount of solvent and given number of stages is appreciably better than when part of the fresh solvent is used in each stage.

The maximum extraction efficiency would be obtained if it were possible to get intimate contact between phases in an apparatus in which the solid phase and the liquid phase passed continuously in opposite directions. True continuous countercurrent extraction is approached in the case of removal of solute from one liquid by another liquid but is difficult to obtain in leaching a solid.

Solvent Extraction Calculation Methods. The two general methods which have received greatest favor for the calculation of solvent extraction problems have been those proposed by Ravenscroft[36] and by Elgin.[13] Both methods make use of graphical solutions. Ravenscroft's method employs rectangular coordinate paper; Elgin's method requires triangular curve paper.

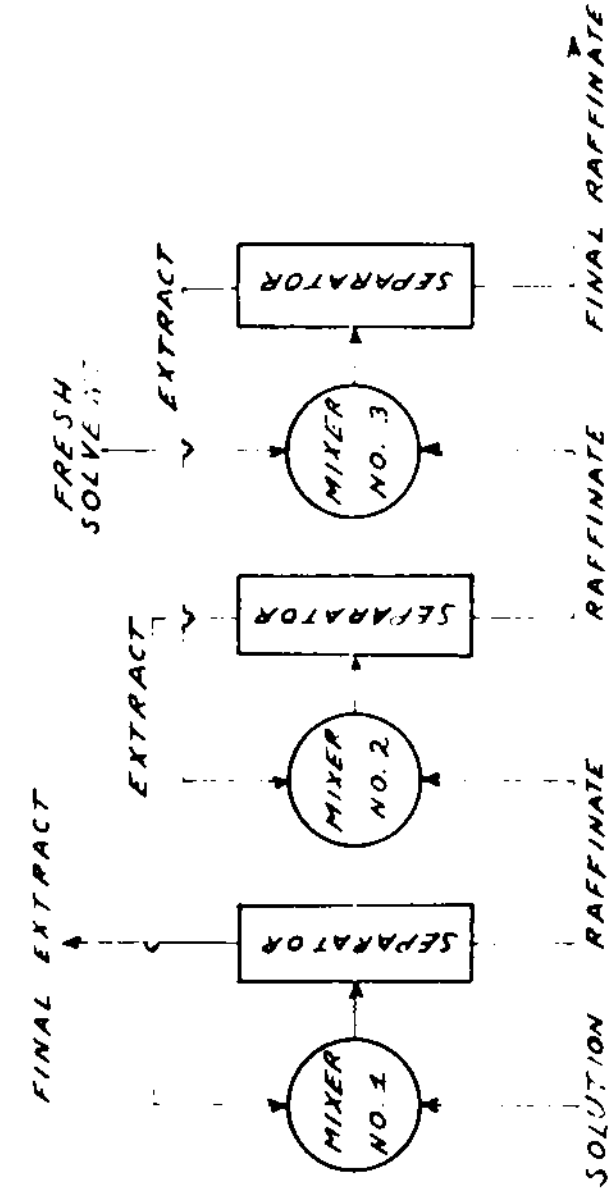


FIGURE 3

THREE-STAGE COUNTERCURRENT MULTIPLE CONTACT EXTRACTION

For the special case in which the retention of the solvent-solute solution by the solute-free inert material is uniform, Baker[2] has developed a method of calculation based upon series relationships.

Equipment for Solvent Extraction. Generally continuous extraction is more adaptable to large scale operation; due to the greater initial cost it is not suitable for small scale operation. The extra cost is somewhat offset by the small operating force required and by the time saved in automatic charging and discharging of the extractor.

Batch extraction, on the other hand, is costlier to operate but has been improved by means of extraction tanks arranged in series. These batteries of tanks are connected by suitable piping so that fresh solvent may be added to any tank and strong solution removed from any tank with the remaining members of the series being kept in countercurrent. Fresh solvent is introduced into the tank containing the solid that is most nearly extracted, flows through the several tanks in series, and is discharged from the tank that has been freshly charged. The material in any one tank remains stationary until extracted.

Apparatus for batch extraction such as the open tank, Dorr classifier, Pachuca tank, etc. are discussed by Badger and McCabe.[1]

Continuous systems for solvent extraction are discussed by Goss[19] and Dean.[10] Goss describes the Hildebrandt extractor, the Bollman system of extraction which is similar

to the French Oil Mill Machinery Company's process, the Allis-Chalmers extractor, the Kennedy extractor, the Ford extractor, and an extractor which is similar to the Ford extractor but is designed for solvents heavier than the oil being extracted (in this case trichlorethylene and soybean oil) being developed by the Iowa State College in conjunction with the R. and H. Chemicals Department of the du Pont Company. Dean discusses the Steinmann, Bamag-Meguin A. G., Schlotterhose and Company, Bighouse, and Fauthsche A. G. extractors.

Many other continuous extractors have been patented and reported in the literature[24] but the ones reviewed by Goss and Dean have received the most extended use.

III. EXPERIMENTAL

A. Purpose and Plan

The purpose of this study was to investigate the efficacies of various solvents for the extraction of tung oil from tung kernels and to determine the applicability of the most efficacious solvent to batch and continuous extraction.

The plan of experimental work was as follows:

1. Preparation of tung nuts for solvent extraction by hulling and grinding.

2. Extraction of ground tung kernels with ethyl alcohol, normal hexane, benzene, toluene, chloroform, and carbon tetrachloride in Soxhlet extractors in order to determine the most effective solvent.

3. Determination of flash points of mixtures of the most efficient flammable and non-inflammable solvents in order to obtain a mixture which would be non-inflammable and would contain the least amount of non-inflammable solvent.

4. Extraction of ground tung kernels with the selected non-inflammable mixture in Soxhlet extractors.

5. Determination of densities of mixtures of the flammable and non-inflammable solvent for varying concentrations.

6. Investigation of the retention of various tung oil-solvent mixtures by oil-free tung meal, the solvent being

the selected non-inflammable mixture, and the oil-free tung meal having been prepared previously by Soxhlet extraction with this same solvent.

7. Batch extraction of raw tung kernels at 10, 22, and 40 deg. C. for 15, 30, 60, and 90 minute extraction periods with the selected non-inflammable solvent mixture.

8. Batch extraction of roasted tung kernels at 22 deg. C. for 15, 30, 60, and 90 minute extraction periods with the same non-inflammable solvent mixture.

9. Investigation of the feasibility of extracting tung kernels with the non-inflammable mixture as a continuous rather than a batch operation.

B. Materials

Benzene. Benzene was obtained by distillation from a benzene - benzoic acid solution which was available in the chemical engineering stock room. The distillate was redistilled and the fraction boiling at 78-79 deg. C. was used in this investigation.

Carbon Tetrachloride. The carbon tetrachloride used in this investigation was of technical grade obtained from the Phipps and Bird Co., Inc., Richmond, Virginia.

Chloroform. Chloroform used in this investigation was of technical grade available in the chemical engineering stock room.

Ethyl Alcohol. Ethyl alcohol used in this investigation was 95 per cent alcohol, scientific grade.

Normal Hexane. Normal hexane used had a boiling point range of 65-70 deg. C. and was purchased from the Fisher Scientific Co., Pittsburgh, Pennsylvania.

Toluene. Toluene was obtained by distillation from a toluene - benzoic acid solution which was available in the chemical engineering stock room. The distillate was redistilled and the fraction boiling at 108-110 deg. C. was used in this investigation.

Tung Nuts. The tung nuts used were those remaining from the investigation which J. T. Castles conducted at the Virginia Polytechnic Institute. Originally one hundred pounds of the 1940 crop of tung nuts had been purchased from Mr. Thigpen of Picayune, Mississippi, at $0.04 per pound.

C. Apparatus

Balance. A chainomatic balance manufactured by Seederer Kohlbusch Inc., Jersey City, New Jersey, was used. The weights for the balance were manufactured by the same company.

Ball Mill. The ball mill used was 12½ inches inside diameter, 18½ inches inside length, and was lined with "Porete".

Density Balance. The Westphal density balance used was purchased from the Fisher Scientific Co., Pittsburgh, Pennsylvania. Since the smallest rider was missing, densities could be determined to only three decimal places without interpolation.

Drying Oven. A 110 volt, 660 watt electric drying oven manufactured by E. H. Sargent and Co., Chicago, Illinois, was used. Serial number 01692.

Extraction Bottles. Eight 250 ml. wide mouth bottles were used without the accompanying ground glass covers for performing batch extractions.

Flash Point Tester. A Cleveland open cup tester conforming to the requirements set forth in "Standard Method of Test for Flash and Fire Points by means of Open Cup", A.S.T.M. Designation D 92-33, was borrowed from the Mechanical Engineering Department of the Virginia Polytechnic Institute and used to determine flash points of binary solvent mixtures.

Food Chopper. A number 45 "Sears Bestmade" food chopper was used with the medium size cutter having 10 holes, each 3/8 inch in diameter. Catalogue number 11E5529.

Pyrex Pipe. A five foot length of Pyrex glass pipe having an inside diameter of 2 inches was used.

Radiant Heat Oven. The heating chamber of the radiant heat oven was 16 inches x 16 inches x 16 inches and was heated by two resistance coils each 660 watts and 110 volts.

Scale. The scale used was labeled Ohaus, Newark, New Jersey. The maximum reading on the scale was 610 grams; the scale weighed to 0.1 gram without interpolation.

Soxhlet Extraction Equipment. The four extraction assemblies, catalogue number S-31225, purchased from E. H. Sargent and Co., Chicago, Illinois, consisted of the following:

a) Four large-size pyrex extractors, 50 mm. inside diameter, 110 mm. siphon tube. Catalogue number 31365.

b) Four Allihn condensers with 250 mm. jackets.

c) Ten 250 ml. pyrex extraction flasks. Catalogue number 34205.

Stirrer Motor. The motor used in stirring the solution containing the kernels for batch extraction was manufactured by Eastern Engineering Co., New Haven, Conn. It was part of an Eastern Laboratory Pump Model C -- 115 v.a.c.

Thimbles. Two sizes of Soxhlet thimbles were used in this investigation. The large size used for extraction purposes was 123 mm. inside length and 43 mm. inside diameter. The small size used to obtain retention data was 80 mm. inside length and 22 mm. inside diameter.

Miscellaneous Equipment. Condensers for recovering solvent, an aspirator for vacuum distillation, two Buchner funnels, vacuum flasks, beakers, flasks, evaporating dishes, oxygen tubes, and other miscellaneous equipment were used.

Batch Extractor. Figure 4 shows the arrangement of the batch extractor for the extractions carried out at 22 deg. C.

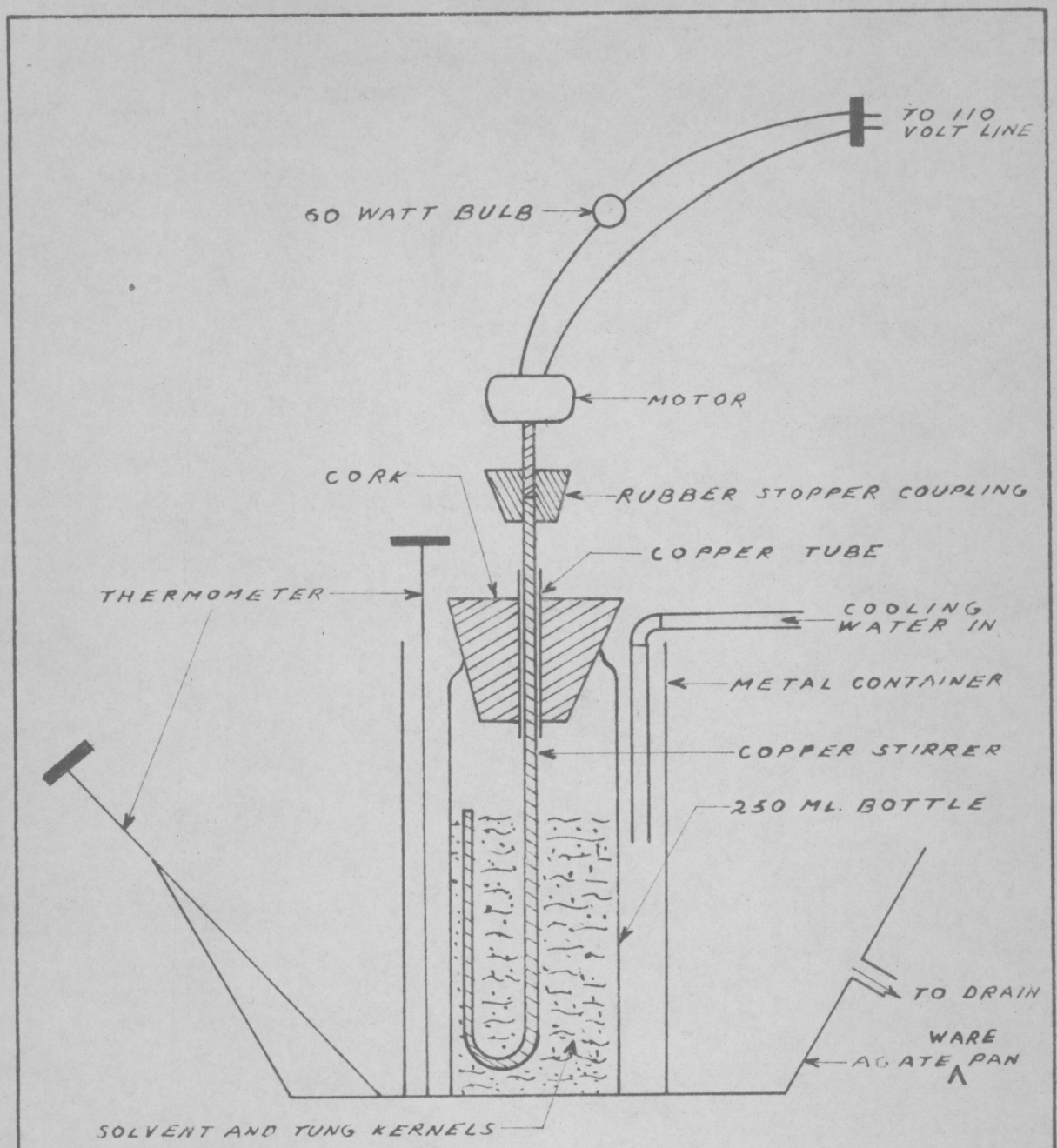


FIGURE 4

BATCH EXTRACTOR

(NOT TO SCALE)

Cooling water flowed into the metal container, overflowed into the agate pan, and flowed out to the drain through a pipe fastened to the side of the pan.

For the 40 deg. C. runs a small hot plate under the agate pan was used to maintain the proper temperature. When the extractions were conducted at 10 deg. C., ice, placed in the annular space between the wide mouth bottle and the metal container, kept the tung nuts and solvent at the correct temperature.

The copper stirrer was coupled to the shaft of the motor by a rubber stopper as indicated in Figure 4. The speed of the motor was decreased by connecting it in series with a 60 watt electric light bulb to a 110 volt outlet.

Countercurrent Extractor. The countercurrent extractor was constructed of a five foot length of pyrex pipe set at an angle of approximately 10 degrees with the horizontal as shown in Figure 5.

The tung kernels were moved through the pyrex pipe by the washers on rod A or rod B.

Retention Equipment. The equipment for obtaining retention data was constructed as illustrated in Figure 6.

D. Method of Procedure

Hulling and Grinding. The shells containing the tung nut kernels were removed from their hulls by cracking with a

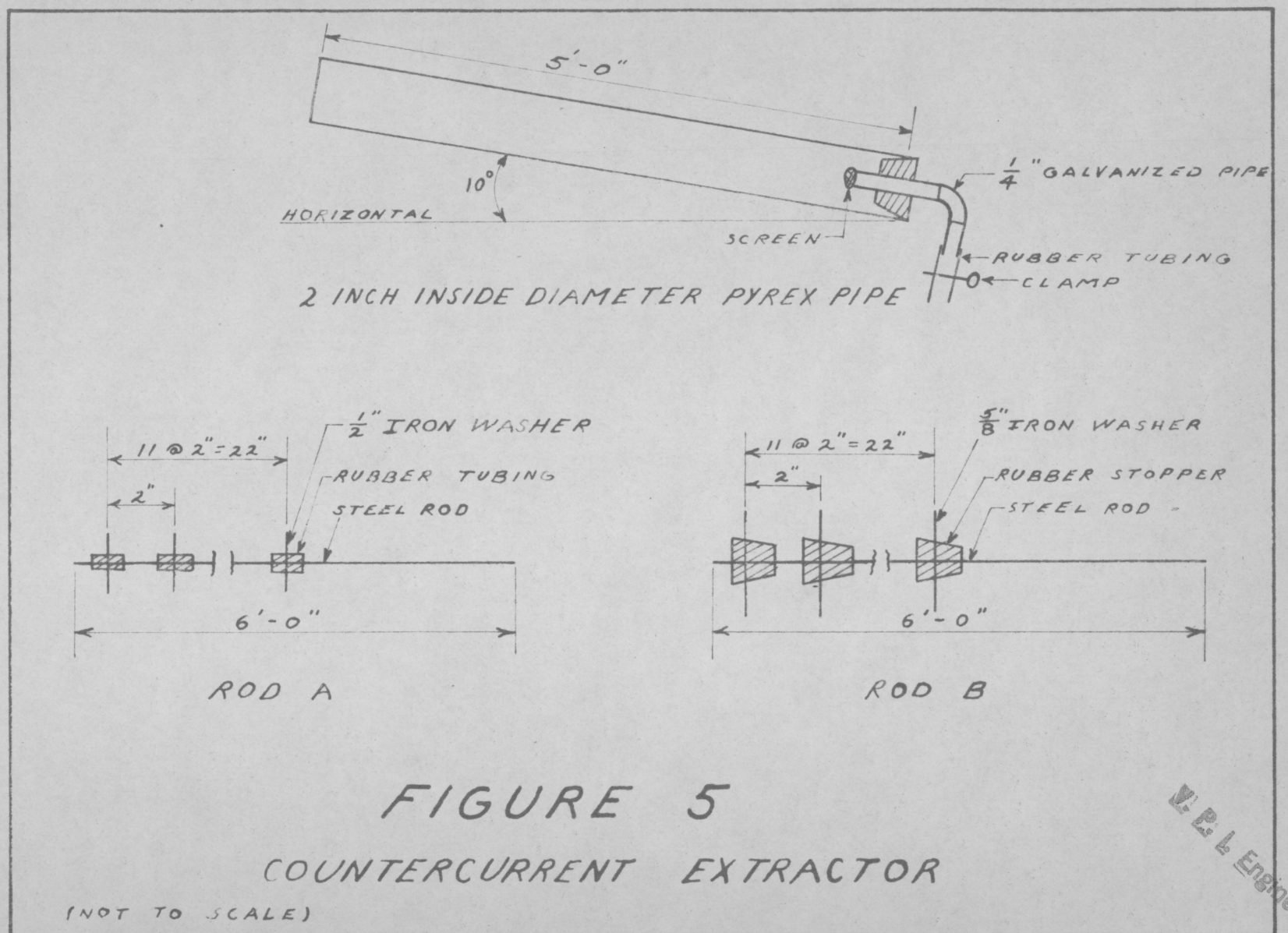


FIGURE 5

COUNTERCURRENT EXTRACTOR

(NOT TO SCALE)

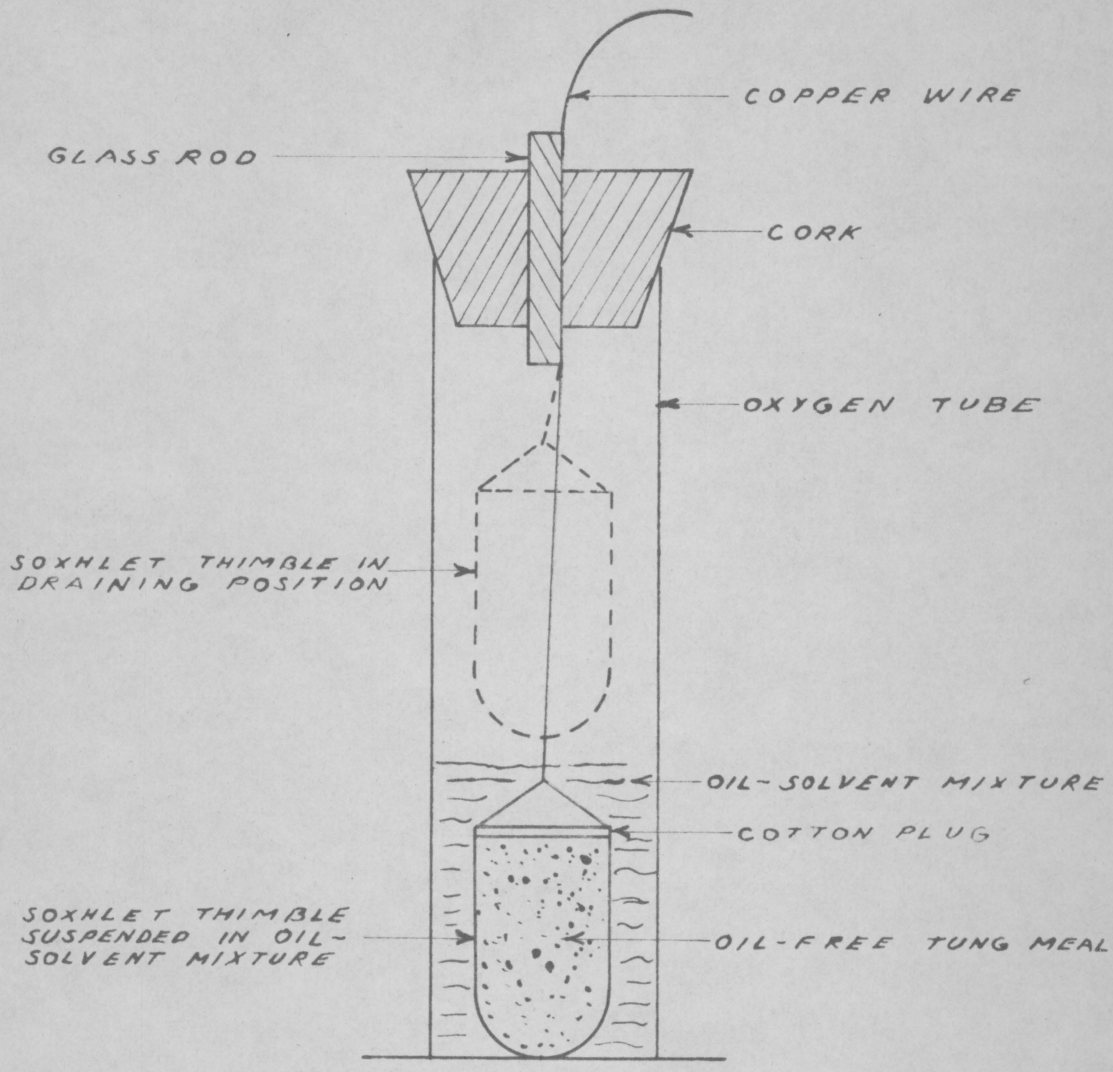


FIGURE 6

RETENTION EQUIPMENT

(NOT TO SCALE)

hammer. They were then placed in a ball mill which was rotated until the outer dusty portion of the shell was worn away. This outer covering was removed in order to prevent contamination of the tung kernels when shelled. Then the shells were broken by a pestle and the tung nut kernels were removed.

Those kernels which had remained intact while being removed from their shells were broken up so that they would not jam the food chopper.

The kernels were ground and reground and were then ready for extraction.

Extraction with Various Solvents. A description of one run will suffice since all runs were the same with the exception of a minor change in the extraction of samples 25, 26, 27, and 28 with the carbon tetrachloride - benzene mixture.

Neustadt[34] found that a Soxhlet extraction could be made more rapidly by raising the thimble off the bottom of the extractor. This was accomplished by inserting a piece of glass rod at an angle on the bottom of the extractor and resting the thimble on the rod.

This was the only change in the extraction of samples 25 to 28, the insertion of a 2 inch (approximately) glass rod in the bottom of the extractor. Otherwise these runs were the same as all the others, a description of which follows:

Approximately a fifty gram sample of ground tung kernels was put into a large-size Soxhlet thimble which had

been weighed previously. (The level of this weight of sample when placed in the extractor was below the top of the siphon leg and hence all the kernels were contacted by solvent.) The kernels and thimble were then weighed accurately on the chainomatic balance and a small wad of cotton was placed on top of the kernels to prevent them from being carried out by solvent. The thimble containing the kernels was then put into the Soxhlet extractor.

A 200 ml. portion of the selected solvent was poured into the extraction flask which was then connected to the Soxhlet extractor. A water-cooled Allihn condenser was attached vertically to the top of the extractor.

Heat was supplied to the flask by a hot plate. Once started, the extraction process continued automatically. Solvent was vaporized in the extraction flask and passed up into the condenser where it condensed and fell down upon the kernels. Whenever the solvent level in the extractor reached the top of the siphon leg, the solvent siphoned back into the flask.

A run was considered to have begun when the first siphonage occurred. The extraction was then continued for eight hours.

After the eight hour extraction period, the flask containing the solvent and extracted tung oil was placed over a hot plate and the solvent distilled off, condensed, and collected. (In the extraction of tung kernels with ethyl

alcohol, the flask containing extracted oil and solvent was heated first in a water bath. However this was later found to be unnecessary since the solutions did not bump when heated over a hot plate if heated carefully.) When the major portion of the solvent had been removed, the extraction flask was placed under vacuum created by an aspirator. The temperature was maintained at 100 to 105 deg. C. and the flask and oil were cooled and weighed at half hour intervals until less than 0.1 gram decrease of weight occurred between two consecutive weighings.

A forty-five minute heating period of the extraction flask under vacuum was found to be sufficient for removal of the solvent.

Flash Point Determinations. The procedure followed was that outlined in "Standard Methods of Test for Flash and Fire Points by Means of Open Cup" A.S.T.M. Designation D 92-33 except that the solvent mixture was heated approximately twice as fast as stipulated in the official test.

Flash point determinations were made upon various carbon tetrachloride - benzene and carbon tetrachloride - hexane mixtures until a solution was obtained of minimum carbon tetrachloride composition which did not flash up to the boiling point of the mixture. A check determination of this final non-inflammable mixture was made in each case.

Densities of Solvent Mixtures. The densities of carbon tetrachloride - benzene mixtures were determined with a

Westphal density balance at 26 deg. C. for compositions ranging from zero per cent to one hundred per cent benzene by volume. The volumes were measured in 50 ml. burettes and the solutions were mixed in 125 ml. Erlenmeyer flasks before densities were determined.

Retention Data. Tung oil obtained by Soxhlet extraction with 70 per cent carbon tetrachloride - 30 per cent benzene by volume was mixed with this same carbon tetrachloride - benzene mixture in varying concentrations from 0.000 to 0.687 gram tung oil per gram of final solution.

Tung kernels which had been extracted with this binary solvent mixture in a Soxhlet extractor were heated in a drying oven at 100 deg. C. for twenty-four hours to remove the solvent. Then 5.00 gram samples of this extracted meal were placed in the small-size Soxhlet thimbles and a small wad of cotton was put over the top of the meal to prevent it from being carried out by the solvent. The various tung oil-solvent mixtures were placed in oxygen tubes and the thimbles containing the extracted kernels, after having been weighed, were suspended in the oil-solvent mixture as shown in Figure 6. After 30 minutes the thimbles were raised and allowed to drain. They drained for 30 minutes and were then weighed.

The thimbles were then soaked in a carbon tetrachloride-benzene mixture for 30 minutes in order to remove the oil retained, were dried in the oven, weighed, and placed back

in the oil-solvent mixture. They were suspended in the solution for 30 minutes and were then allowed to drain for 30 minutes after which time they were again weighed.

Roasting of Tung Kernels. Tung kernels were roasted in the radiant heater for 10 minutes at 199 deg. C. They were then ground twice in the food chopper before extracting.

Note: Batch extraction at 22 deg. C. of samples 44, 45, 46, and 47 were the only experiments conducted on roasted kernels. All other work was conducted on raw tung kernels.

Moisture Determinations. Approximately twenty gram samples of undamaged whole kernels were weighed out accurately in evaporating dishes and dried in the electric drying oven at 101 to 102 deg. C. for 24 hours.

Batch Extraction. One hundred and seventy-five ml. of a 70 per cent carbon tetrachloride - 30 per cent benzene solution by volume were poured into a 250 ml. wide mouth bottle. The solvent was now cooled or heated to the temperature of the test. Thirty grams of tung kernels (ground twice) were placed in the wide mouth bottle, the stirrer was started, and the extraction continued for the selected length of time.

Extractions were carried out at 10 deg. C. using ice, at 22 deg. C. using cooling water, and at 40 deg. C. with the heat furnished by a hot plate. (Figure 4 is a diagram of the apparatus.) Upon completion of the extraction the mixture

was allowed to settle for fifteen minutes.

Then the mixture was filtered through a Buchner funnel and the filtrate poured into a previously weighed extraction flask. The flask and filtrate were weighed. Then the solvent was distilled off from the oil first at atmospheric pressure and then under a vacuum as described previously. The final weight of oil and flask was recorded after removal of the solvent.

Countercurrent Extraction. Tung kernels which had been ground twice were placed in the pyrex pipe. The kernels were moved by washers mounted on a rod. (See Figure 5.) Solvent flowed in a direction opposite to the flow of kernels. Rods containing 1/2 inch and 5/8 inch iron washers were tested.

E. Data and Results

Soxhlet Extraction Yields. The results of extraction of tung kernels with ethyl alcohol, normal hexane, benzene, toluene, chloroform, carbon tetrachloride, and a 70 per cent carbon tetrachloride - 30 per cent benzene mixture by volume are summarized in Tables I to VII inclusive. Average values for the percentages of oil removed with the original samples as bases are given for each of the solvents.

TABLE I

Extraction of Tung Kernels with Ethyl Alcohol

Sample Number	Weight of Sample grams	Yield of Oil grams	Oil Removed-Basis: Original Sample per cent
1	55.11	14.09	25.6
2	54.95	12.94	23.6
3	52.94	12.79	24.2
4	50.29	12.34	24.5
		Average	24.5

TABLE II

Extraction of Tung Kernels with Normal Hexane

Sample Number	Weight of Sample grams	Yield of Oil grams	Oil Removed-Basis: Original Sample per cent
5	50.13	25.46	50.8
6	50.14	25.82	51.5
7	50.57	25.66	50.7
8	50.12	25.05	50.0
		Average	50.8

TABLE III

Extraction of Tung Kernels with Benzene

Sample Number	Weight of Sample grams	Yield of Oil grams	Oil Removed-Basis: Original Sample per cent
9	51.22	26.37	51.5
10	52.53	27.53	52.4
11	50.38	26.22	52.0
12	54.18	27.45	50.7
		Average	51.7

TABLE IV

Extraction of Tung Kernels with Toluene

Sample Number	Weight of Sample grams	Yield of Oil grams	Oil Removed-Basis: Original Sample per cent
13	53.31	27.33	51.3
14	52.72	25.50	48.4
15	56.41	28.46	50.4
16	56.92	-----	----
		Average	50.0

TABLE V

Extraction of Tung Kernels with Chloroform

Sample Number	Weight of Sample grams	Yield of Oil grams	Oil Removed-Basis: Original Sample per cent
17	51.59	-----	----
18	50.64	22.07	43.6
19	53.20	21.94	41.2
20	52.55	22.14	42.1
		Average	42.3

TABLE VI

Extraction of Tung Kernels with Carbon Tetrachloride

Sample Number	Weight of Sample grams	Yield of Oil grams	Oil Removed-Basis: Original Sample per cent
21	51.96	25.72	49.5
22	52.72	24.63	46.7
23	51.82	23.60	45.5
24	52.26	25.98	49.7
		Average	47.8

TABLE VII

Extraction of Tung Kernels with a Mixture of 70 Per Cent Carbon Tetrachloride - 30 Per dent Benzene (by Volume)

Sample Number	Weight of Sample grams	Yield of Oil grams	Oil Removed-Basis: Original Sample per cent
25	50.46	26.14	51.8
26	52.44	26.94	51.4
27	51.20	-----	----
28	51.32	26.00	50.7
		Average	51.3

Flash Points of Solvent Mixtures. Tables VIII and IX give the flash points of carbon tetrachloride - hexane and carbon tetrachloride - benzene mixtures respectively.

TABLE VIII

Flash Points of Carbon Tetrachloride - Hexane Mixtures

Carbon Tetrachloride per cent by volume	Hexane per cent by volume	Flash Point deg. F.
70	30	85
80	20	85
83	17	150
85	15	(none up to boiling)

TABLE IX

Flash Points of Carbon Tetrachloride - Benzene Mixtures

Carbon Tetrachloride per cent by volume	Benzene per cent by volume	Flash Point deg. F.
65	35	120
68	32	(none up to boiling)
70	30	(none up to boiling)

Densities of Carbon Tetrachloride - Benzene Mixtures.

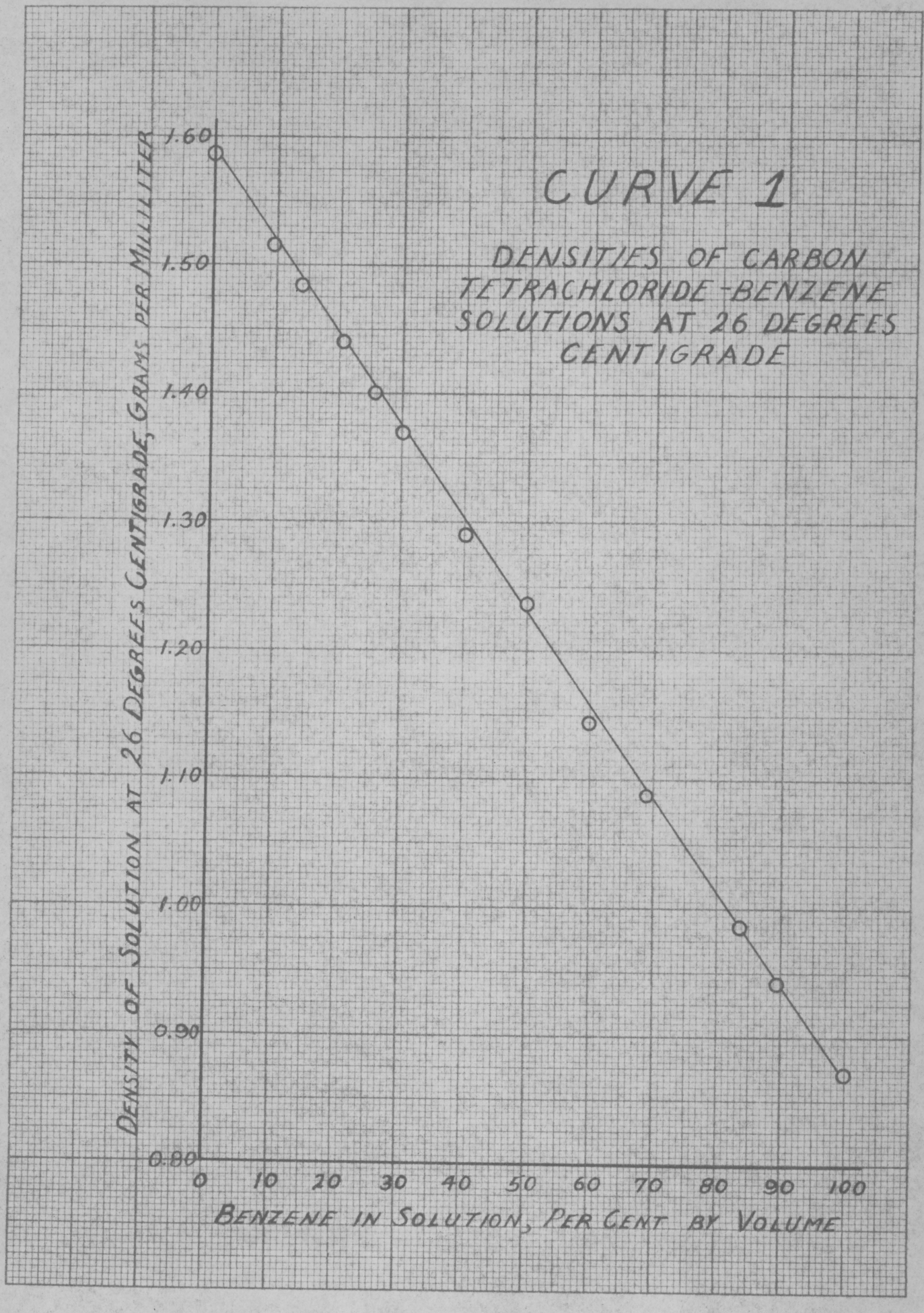
The densities in gm. per ml. at 26 deg. C. are given for carbon tetrachloride - benzene mixtures in Table X for mixtures of the two solvents ranging in composition from pure carbon tetrachloride to pure benzene.

Curve 1 is a plot of these data with the volume per cent of benzene in the solution plotted as the abscissa and the density of the solution at 26 deg. C. in gm. per ml. as the ordinate.

TABLE X

Densities of Carbon Tetrachloride-Benzene Mixtures at 26 deg. C.

Carbon Tetrachloride ml.	Benzene ml.	Compositions of Mixtures (by Volume)		Density gm./ml.
		Carbon Tetrachloride per cent	Benzene per cent	
0.0	50.0	0.0	100.0	0.872
5.3	45.9	10.4	89.6	0.942
8.5	43.1	16.5	83.5	0.986
15.5	34.8	30.8	69.2	1.089
20.0	30.0	40.0	60.0	1.144
25.0	25.0	50.0	50.0	1.237
30.0	20.2	59.8	40.2	1.290
35.0	15.0	70.0	30.0	1.371
37.0	13.0	74.0	26.0	1.400
39.0	10.0	79.6	20.4	1.439
43.0	7.0	86.0	14.0	1.484
45.4	5.0	90.1	9.9	1.515
50.0	0.0	100.0	0.0	1.587


CURVE 1
DENSITIES OF CARBON TETRACHLORIDE-BENZENE SOLUTIONS AT 26 DEGREES CENTIGRADE
DENSITY OF SOLUTION AT 26 DEGREES CENTIGRADE, GRAMS PER MILLILITER
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0
10
20
30
40
50
60
70
80
90
100
BENZENE IN SOLUTION, PER CENT BY VOLUME

Conversion of Volume Per Cent to Weight Per Cent. The relationships between the percentages by volume and the percentages by weight of carbon tetrachloride - benzene mixtures at 26 deg. C. are given in Table XI for mixtures of the two solvents ranging in composition from pure carbon tetrachloride to pure benzene.

TABLE XI

Relationships between Percentages by Volume and by Weight of Carbon Tetrachloride - Benzene Mixtures at 26 deg. C.

Composition of Mixture by Volume		Composition of Mixture by Weight	
Carbon Tetrachloride per cent	Benzene per cent	Carbon Tetrachloride per cent	Benzene per cent
0.0	100.0	0.0	100.0
10.4	89.6	17.4	82.6
16.5	83.5	26.4	73.6
30.8	69.2	44.8	55.2
40.0	60.0	54.8	45.2
50.0	50.0	64.6	35.4
59.8	40.2	73.0	27.0
70.0	30.0	81.0	19.0
74.0	26.0	83.8	16.2
79.6	20.4	87.6	12.4
86.0	14.0	91.8	8.2
90.1	9.9	94.3	5.7
100.0	0.0	100.0	0.0

Addition of Solvent to Give a Non-Inflammable Mixture.

Data are given in Table XII for the ml. of carbon tetrachloride and the ml. of benzene necessary per 100 ml. of solution of given density to form a solution having a final composition of 70 per cent carbon tetrachloride - 30 per cent benzene by volume.

TABLE XII

Addition of Solvents to Various Mixtures to Give a Solution Having a Composition 70 Per Cent Carbon Tetrachloride - 30 Per Cent Benzene by Volume at 25 deg. C.

Density gm./ml.	Carbon Tetrachloride Necessary per 100 ml. of Solution ml.	Benzene Necessary per 100 ml. of Solution ml.
0.872	233.3	0.0
0.942	198.7	0.0
0.986	178.3	0.0
1.089	130.7	0.0
1.144	100.0	0.0
1.237	66.7	0.0
1.290	34.0	0.0
1.371	0.0	0.0
1.400	0.0	5.7
1.439	0.0	13.7
1.484	0.0	22.9
1.515	0.0	28.7
1.587	0.0	42.9

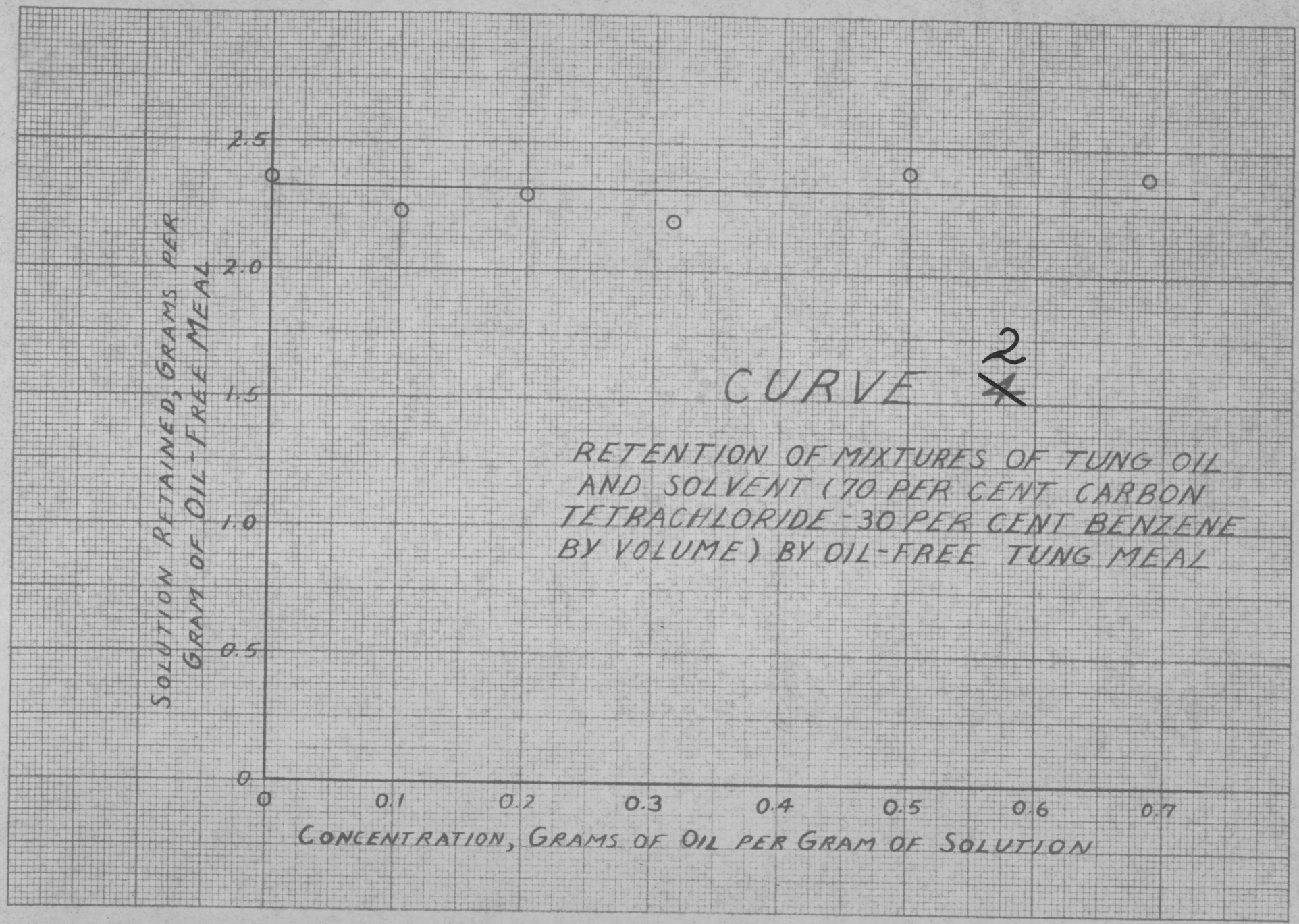
Retention of Tung Oil by Tung Meal. The relationships between the gm. of solution retained per gm. of oil-free meal and the concentrations of the solutions in gm. of oil per gm. of solution are given in Table XIII.

Curve 2 is a plot of these data with concentration as the abscissa and solution retained as the ordinate.

TABLE XIII

Retention of Mixtures of Tung Oil and Solvent (70 per cent Carbon Tetrachloride - 30 per cent Benzene by Volume) by Oil-Free Tung Meal

Concentration gm. oil per gm. solution	Density gm./ml.	Solution Retained by 5 gm. Oil-Free Meal and Thimble gm.	Solution Retained by Thimble gm.	Solution Retained per gm. Oil-Free Meal gm.
0.000	1.371	14.68	2.91	2.36
0.100	1.308	14.43	3.07	2.27
0.200	1.258	13.86	2.39	2.29
0.314	1.199	14.00	3.06	2.19
0.500	1.116	15.06	3.11	2.39
0.687	1.043	15.16	3.27	2.38



CURVE 2

RETENTION OF MIXTURES OF TUNG OIL AND SOLVENT (70 PER CENT CARBON TETRACHLORIDE - 30 PER CENT BENZENE BY VOLUME) BY OIL-FREE TUNG MEAL

Roasting of Tung Kernels. Table XIV shows the loss in weight sustained by the tung kernels upon roasting under the conditions given in the section "Method of Procedure".

Moisture Content of Tung Kernels. The percentages of moisture present in three samples of tung kernels are averaged in Table XV.

TABLE XIV

Roasting of Tung Kernels

Length of roasting (min.)	10
Temperature of radiant heater (deg. C.)	199
Weight of kernels before roasting (gm.)	206.8
Weight of kernels after roasting (gm.)	200.3
Loss in weight of kernels (gm.)	6.5
Loss in weight of original sample (per cent)	3.14

TABLE XV

Moisture Content of Tung Kernels

Temperature of drying oven (deg. C.) ---------- 101 to 102

Length of drying (hours) ---------- 24

Sample Number	Weight of Kernels before Drying gm.	Weight of Dried Kernels gm.	Loss in Weight of Kernels gm.	Moisture in Original Sample per cent
29	20.206	19.661	0.545	2.70
30	20.282	19.714	0.568	2.81
31	20.621	20.026	0.595	2.89
			Average	2.80

Batch Extraction of Tung Kernels. Tables XVI, XVII, and XVIII show the results obtained in the batch extraction of raw tung kernels at 10, 22, and 40 deg. C. with extraction periods of 15, 30, 60, and 90 minutes. Results are expressed in gm. of oil per gm. of solution and efficiency of extraction in per cent.

Results are expressed similarly in Table XIX for the batch extraction of roasted tung kernels at 22 deg. C. with the same extraction periods of 15, 30, 60, and 90 minutes.

The data tabulated in Tables XVI to XIX inclusive are plotted in Curve 3 with a separate curve for each table. Length of extraction in minutes is plotted as the abscissa and efficiency of extraction in per cent as the ordinate.

TABLE XVI

Batch Extraction of Raw Tung Kernels at 10 deg. C.

Weight of raw kernels (gm.) ---------- 30

Solvent Used ---- 70 per cent carbon tetrachloride - 30 per cent benzene (by volume)

Volume of solvent (ml.) ---------- 175

Sample Number	Length of Extraction min.	Concentration gm. Oil per gm. Solution	Efficiency of Extraction per cent
32	15	0.0404	67.0
33	30	0.0410	68.0
34	60	0.0425	70.5
35	90	0.0435	72.1

TABLE XVII

Batch Extraction of Raw Tung Kernels at 22 deg. C.

Weight of raw kernels (gm.) ---------- 30

Solvent Used ---- 70 per cent carbon tetrachloride - 30 per cent benzene (by volume)

Volume of solvent (ml.) ---------- 175

Sample Number	Length of Extraction min.	Concentration gm. Oil per gm. Solution	Efficiency of Extraction per cent
36	15	0.0466	77.3
37	30	0.0483	80.1
38	60	0.0525	87.1
39	90	0.0562	93.2

TABLE XVIII

Batch Extraction of Raw Tung Kernels at 40 deg. C.

Weight of raw kernels (gm.) ---------- 30

Solvent Used ---- 70 per cent carbon tetrachloride - 30 per cent benzene (by volume)

Volume of solvent (ml.) ---------- 175

Sample Number	Length of Extraction min.	Concentration gm. Oil per gm. Solution	Efficiency of Extraction per cent
40	15	0.0491	81.4
41	30	0.0508	84.3
42	60	0.0546	90.6
43	90	0.0579	96.0

TABLE XIX

Batch Extraction of Roasted Tung Kernels at 22 deg. C.

Weight of roasted kernels (gm.) -------- 30

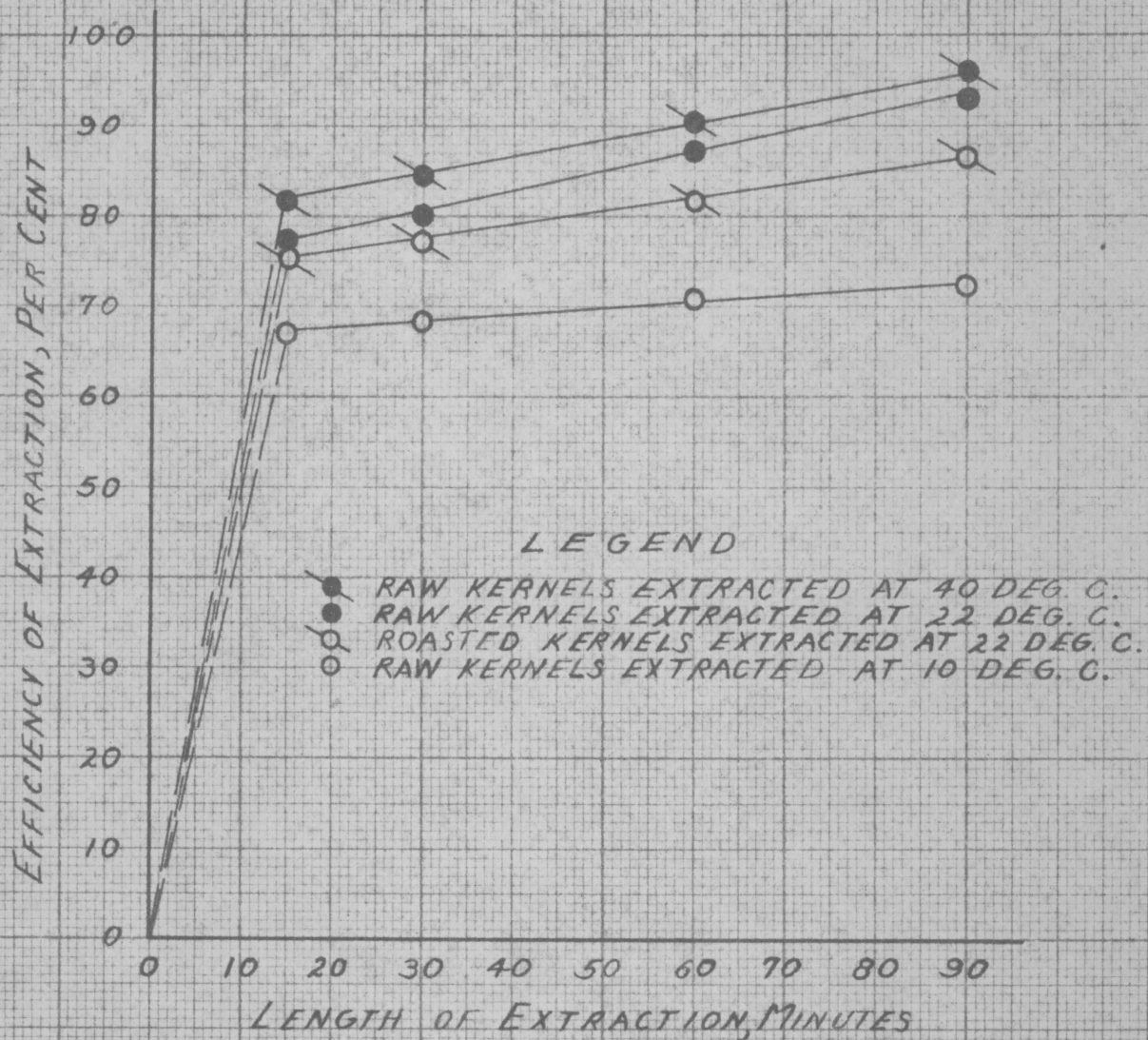
Solvent Used ---- 70 per cent carbon tetrachloride - 30 per cent benzene (by volume)

Volume of solvent (ml.) ---------- 175

Sample Number	Length of Extraction min.	Concentration gm. Oil per gm. Solution	Efficiency of Extraction per cent
44	15	0.0467	75.2
45	30	0.0481	77.4
46	60	0.0507	81.6
47	90	0.0537	86.5

CURVE 13

EFFICIENCIES OF BATCH EXTRACTIONS OF 30 GRAMS OF TUNG KERNELS WITH 175 MILLILITERS OF A 70 PER CENT CARBON TETRACHLORIDE - 30 PER CENT BENZENE SOLUTION (BY VOLUME)



IV. DISCUSSION

A. Discussion of Results

Soxhlet Extraction With Various Solvents. Carbon tetrachloride was selected as the non-inflammable solvent to use in preparing a non-inflammable mixture because it was found to be more effective than chloroform for the extraction of tung kernels in a Soxhlet extractor. Of the total weight of kernel, 47.8 per cent was recovered as oil by carbon tetrachloride. Chloroform recovered only 42.3 per cent oil.

In the flammable solvent class, benzene extracted 51.7 per cent oil, normal hexane 50.8 per cent, toluene 50.0 per cent and ethyl alcohol 24.5 per cent.

All the solvent-oil mixtures which were obtained were miscible with the exception of the alcohol-oil mixture which separated into two layers upon cooling. According to Goss[19] ethanol and also methanol are examples of a considerable group of solvents which display partial miscibility with glyceride-type fats and oils at low temperatures.

However this property of ethanol-oil mixtures was not considered to be a serious factor in selecting a flammable solvent to use as one of the members of a non-inflammable mixture since ethyl alcohol has been used successfully to extract soybean oil commercially. In this so-called hot

alcohol process, ethanol under pressure at 80 deg. C. is used to extract soybean oil in a battery of rotary extractors. When the resulting miscella is cooled to room temperature, an alcohol-rich and an oil-rich phase result. The alcohol-rich layer is re-used, and the oil-rich layer is separated by distillation. Ethyl alcohol was eliminated principally because of its low extractive powers.

Toluene gave a satisfactory yield of oil which was slightly below the yields obtained with hexane and benzene. However the high boiling point of toluene, 110.8 deg. C., indicated that complete recovery of solvent from the resulting toluene-tung oil solution would be difficult. Consequently toluene was eliminated from further investigation.

The amount of oil extracted with benzene was only slightly greater than that extracted with hexane and, for all practical purposes, the effectiveness of both solvents was considered equal.

Therefore the final choice of non-inflammable solvent mixture was between carbon tetrachloride - benzene and carbon tetrachloride - hexane.

Flash Point Determinations. In order to determine the minimum concentrations of carbon tetrachloride necessary to produce non-inflammable mixtures, flash point determinations were made of various carbon tetrachloride - benzene and carbon tetrachloride - hexane mixtures. A 70 per cent carbon tetrachloride - 30 per cent benzene mixture by volume and a

85 per cent carbon tetrachloride - 15 per cent hexane mixture by volume were found to be non-inflammable.

Cost analyses of these two mixtures showed that the carbon tetrachloride - benzene mixture was the cheaper of the two. ("Selection of Non-Inflammable Solvent Mixture", section A, of the appendix, gives a summary of the calculations involved.) Consequently this mixture was selected for further investigation.

When tung kernels were extracted in Soxhlet extractors with this 70 per cent carbon tetrachloride - 30 per cent benzene mixture, a tung oil content in the original kernel of 51.5 per cent was indicated. Since benzene had extracted 51.7 per cent oil when used alone, this non-inflammable mixture was considered to be equally effective.

Densities of Carbon Tetrachloride - Benzene Mixtures. The curve of densities of carbon tetrachloride - benzene solutions plotted against the benzene concentrations of the solutions (Curve 1) is a straight line function.

Conversion of Volume Per Cent to Weight Per Cent. Curve 4, a plot of the percentages by volume of carbon tetrachloride-benzene mixtures against the percentages by weight of these mixtures, slopes upward as plotted, showing that for a given increase in the benzene percentage by volume, the corresponding benzene percentage by weight does not increase as rapidly since benzene is less dense than carbon tetra-

chloride, having a density only fifty-five per cent that of carbon tetrachloride.

Addition of Solvents to Give a Non-Inflammable Mixture. The data given in Table XII and Curve 5, a plot of these data, may readily be used in determining the amount of carbon tetrachloride or benzene to be added to a given solution in order to obtain the final non-inflammable mixture.

Retention of Tung Oil by Meal. Curve 2, the curve of solvent-oil solution retention by the meal as a function of the concentration of the solution is plotted as a straight line. A straight line plot is justifiable since it is within the accuracy of the investigation and since no definite trend is apparent in the data as plotted.

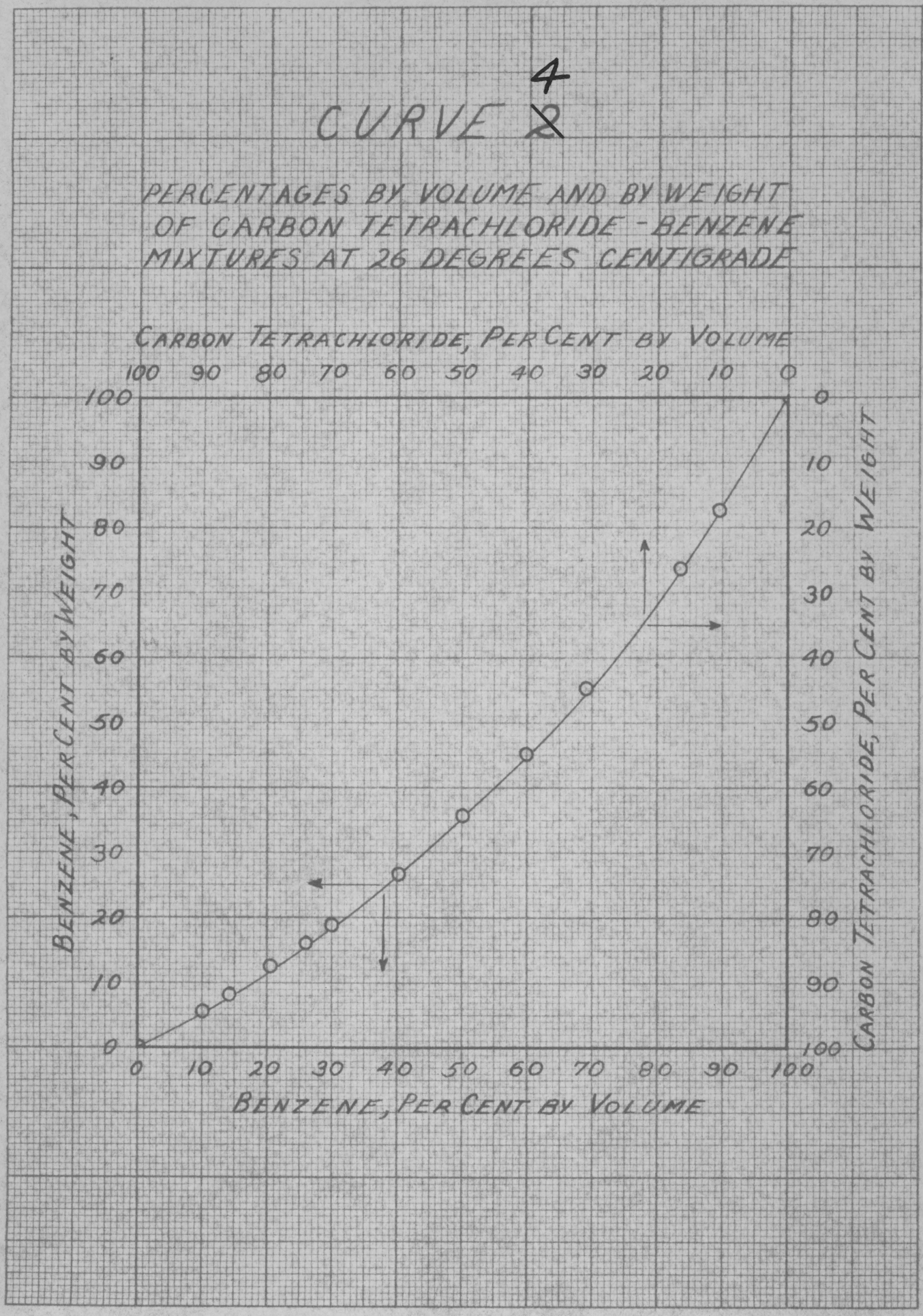
The use of this curve in predicting maximum theoretical extraction yields is discussed in section C of the appendix, "Prediction of Extraction Yields."

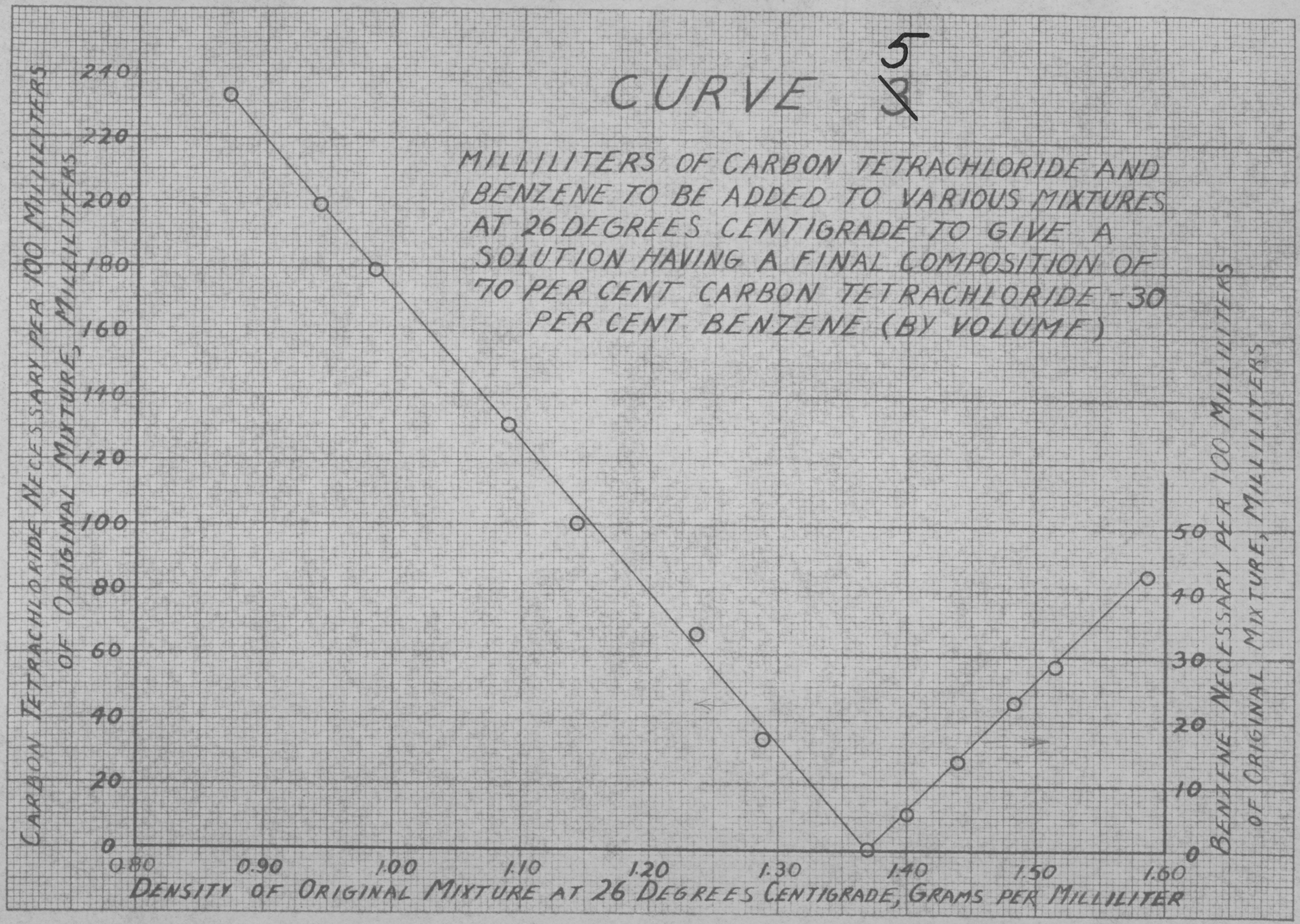
Batch Extraction. The results of the batch extraction of raw tung kernels at 10, 22, and 40 deg. C. and of roasted tung kernels at 22 deg. C. with 70 per cent carbon tetrachloride - 30 per cent benzene for 15, 30, 60, and 90 minute periods are summarized in Curve 3.

These were batch extractions and consequently they definitely limited the amount of oil that could be removed in any one operation. Therefore, as plotted, 100 per cent efficiency of extraction would not mean that all the oil in the kernel could be removed since some would be present in

CURVE ~~2~~ 4

PERCENTAGES BY VOLUME AND BY WEIGHT OF CARBON TETRACHLORIDE - BENZENE MIXTURES AT 26 DEGREES CENTIGRADE




CURVE 5
MILLILITERS OF CARBON TETRACHLORIDE AND BENZENE TO BE ADDED TO VARIOUS MIXTURES AT 26 DEGREES CENTIGRADE TO GIVE A SOLUTION HAVING A FINAL COMPOSITION OF 70 PER CENT CARBON TETRACHLORIDE - 30 PER CENT BENZENE (BY VOLUME)
CARBON TETRACHLORIDE NECESSARY PER 100 MILLILITERS OF ORIGINAL MIXTURE, MILLILITERS
BENZENE NECESSARY PER 100 MILLILITERS OF ORIGINAL MIXTURE, MILLILITERS
0 20 40 60 80 100 120 140 160 180 200 220 240
0 10 20 30 40 50
0.80 0.90 1.00 1.10 1.20 1.30 1.40 1.50 1.60
DENSITY OF ORIGINAL MIXTURE AT 26 DEGREES CENTIGRADE, GRAMS PER MILLILITER

the solution retained by the meal. Rather, 100 per cent efficiency of extraction means that all the oil that theoretically could be removed in a single batch operation under the given conditions of weight of solvent used, weight of kernels used, etc., was removed.

The curves show regular properties with the efficiency of extraction increasing with increased temperatures for the raw tung nuts up to a 96.0 per cent efficiency for a 90 minute extraction at 40 deg. C.

Roasted tung kernels were extracted only at 29 deg. C. since comparison of the results obtained with those results obtained for the extraction of raw kernels at the same temperature showed that the efficiency of the extraction was less for the roasted kernels and consequently there was no justification in roasting the tung kernels.

Countercurrent Extraction. Since countercurrent extraction is decidedly more economical than batch extraction, several tests were conducted in order to determine how well the tung kernels would handle in a countercurrent extractor.

Several types of countercurrent extractors appeared to be applicable to tung oil extraction:

1. The Allis-Chalmers extractor is a vertical cylindrical column containing a central rotating shaft fitted with a series of horizontal slotted plates. Stationary scraper arms cause the solid material to fall from one slowly rotating plate to another descending against an upward solvent stream.

As such the Allis-Chalmers extractor is not suited for the extraction of tung kernels with the carbon tetrachloride - benzene mixture under investigation since the ground tung kernels floated when placed in the solvent mixture.

This Allis-Chalmers vertical extractor might be modified so that a vertical screw would carry kernels from the bottom of the chamber to the top. (This is somewhat similar to the Hildebrandt extractor.) For countercurrent flow the solvent would now travel downward. But the density of the oil-solvent solution decreases as the concentration of oil in the solution increases. Therefore this apparatus would not operate properly since the tendencies of the oil and the oil-solvent solutions formed would be to rise instead of fall.

2. An extractor developed from work by the Iowa State College and by the R. and H. Chemicals Department of the du Pont Company is designed for solvents heavier than the oil being extracted. It is similar in construction to a Ford extractor but the materials flow is reversed. This "reversed Ford" extractor makes use of an inclined tube housing an internal screw which conveys beans downward against a countercurrent upward solvent flow.

A preliminary test of the feasibility of using such an apparatus was made with the equipment sketched in Figure 5. Tung kernels and solvent were placed in the pyrex pipe

and rod A was inserted. The kernels floated to the top of the pyrex pipe and rod A was not effective in propelling the kernels. Rod B which contained larger washers and thus reduced the area of the annular space between the washers and the inside of the pipe was then tried. Again difficulty was encountered due to the kernels floating to the top.

B. Recommendations

The following recommendations are made for future work on this subject:

Effect of Water Content on Solvent Extraction. Conflicting reports appear in the literature as to the effect of the presence of moisture in seeds upon solvent extraction. Investigation along this line should be made.

Dean[11] reports that seeds are usually prepared for solvent extraction by drying. "This drying is necessary because of the strong repelling action of the hydrophilic moist cells on the hydrophobic solvent."

Lewkowitsch[2b] on the other hand states that the warming of the seed preliminary to its treatment with volatile solvents is unnecessary, "as the moisture contained in the seed does not offer a serious obstacle to thorough extraction."

Effect of Kernel Size upon Extraction. Tung kernels were prepared by grinding in this investigation. Future studies should be made of the effect of particle size and possibly the effect of shape of particle upon extraction. The optimum sizes and shapes of tung kernels for extraction should be determined.

Corrosive Action of Chlorinated Hydrocarbons. One of the serious objections to the use of chlorinated hydrocarbons has been the fact that they decompose upon heating, especially in the presence of moisture, liberating hydrogen chloride which attacks iron and copper. Protection can be secured with relatively expensive lead-lined and tinned equipment. This corrosive action of the chlorinated hydrocarbons suggests several studies:

1. According to Lewkowitsch,(26) the addition of oil of turpentine, which absorbs hydrochloric acid, "is said to obviate the destructive effect on iron." Perhaps benzene, in the presence of carbon tetrachloride, will act similarly or will inhibit the corrosive action of carbon tetrachloride. It is possible that 70 per cent carbon tetrachloride - 30 per cent benzene by volume, in addition to being non-inflammable, may also be much less corrosive than carbon tetrachloride alone. Studies should be made of this phase of tung oil extraction.

2. Trichlorethylene is the most stable of the chlorinated hydrocarbons. According to Goss,(19) equipment designed for trichlorethylene is now on the market. Among

the disadvantages of the chlorinated compounds, "the most serious appears to be the present relatively high price."

The use of benzene admixed with carbon tetrachloride has not only reduced the cost but has also decreased the density of the solvent thus requiring less weight of solvent for a given extraction. Similar mixtures of trichlorethylene with flammable solvents such as benzene, hexane, etc. should be studied.

Continuous Extraction. Further studies should be made of the feasibility of extracting tung oil in some continuous apparatus. For example, it appears feasible that a Bollman type of extractor might be modified so as to be applicable to tung oil extraction with a carbon tetrachloride - benzene mixture. The Bollman type extractor consists of a series of sieve-bottomed baskets which are carried through the system on endless chains. The material to be extracted is charged into the basket and is sprayed with solvent during its passage through the extractor.

Pilot Plant. When most of these preliminary investigations have been completed, studies should be made using extraction apparatus duplicating commercial operation since the engineering problems in the solvent extraction of tung kernels will be solved only by empirical methods.

For example, in the small-scale operations conducted in this investigation, hand-picked samples were used. All rotted and diseased kernels were discarded. Such meticulous care will not be possible on a commercial scale and extraction efficiencies may suffer.

Then too, solvent extraction of tung oil can be compared to mechanical expression only when the extractors and the expression equipment are both operating under conditions of industrial practice upon samples which are as nearly alike as possible.

Solvent Extraction of Tung Meal. Because of the rather high cost of solvent extraction equipment, the seasonal character of the tung oil industry, the fact that there is ample pressing equipment in this country, and because oil millers do not wish to discard their present costly equipment and go to the added expense of installing solvent extraction plants; difficulties will be encountered in converting the tung oil industry over to solvent extraction.

In view of these anticipated difficulties in converting the industry, the United States Department of Agriculture has experimented with the solvent extraction of the tung meal remaining after pressing.

Solvent extraction of tung meal offers possibilities for future study.

V. CONCLUSIONS

From the results of this investigation the following conclusions were drawn:

1. In the Soxhlet extraction of samples of tung kernels from a 1940 Louisiana crop, benzene recovered the greatest amount of oil, 51.7 per cent. The percentages of oil removed from the kernels with the other solvents were normal hexane, 50.8 per cent; toluene, 50.0 per cent; carbon tetrachloride, 47.8 per cent; chloroform, 42.3 per cent; and ethyl alcohol, 24.5 per cent.

2. Solutions consisting of 85 per cent carbon tetrachloride - 15 per cent hexane by volume and 70 per cent carbon tetrachloride - 30 per cent benzene by volume did not flash when heated up to 71 deg. C. and 77 deg. C. (the boiling points of the solutions respectively) in a Cleveland open cup tester.

3. Based upon the assumption that solvent requirements and losses for tung oil extraction would be about the same as for soybean oil extraction, per ton of tung kernels extracted, the initial cost of the non-inflammable carbon tetrachloride - benzene mixture would be $130.89, the carbon tetrachloride - hexane mixture $151.00, and pure carbon tetrachloride when used alone $172.00. Similarly the cost of solvent lost per ton of kernels extracted would be $1.06, $1.14, and $1.20 respectively for each of the three above. Consequently the

carbon tetrachloride - benzene mixture was selected for experimentation.

4. Soxhlet extraction with a 70 per cent carbon tetrachloride - 30 per cent benzene mixture by volume recovered 51.3 per cent oil.

5. The retention of solutions of tung oil and a 70 per cent carbon tetrachloride - 30 per cent benzene mixture by volume for concentrations ranging from 0.000 to 0.687 grams of oil per gram of solution was approximated as 2.32 grams of solution per gram of oil-free tung meal. (The meal had previously been extracted with this same binary mixture.)

6. The efficiencies for batch extractions at 22 deg. C. (with a 70 per cent carbon tetrachloride - 30 per cent hexane mixture by volume) of roasted tung kernels were not as great as those for raw tung kernels at the same temperature.

7. The most efficient extraction of tung kernels with a 70 per cent carbon tetrachloride - 30 per cent benzene mixture by volume was obtained at 40 deg. C. for the batch extraction of raw tung kernels for 90 minutes. A 96 per cent extraction efficiency resulted.

8. The tung kernels, as prepared, floated or remained suspended in the carbon tetrachloride - benzene solution. Therefore an extractor which depends upon the settling of tung kernels countercurrent to the upward flow of solvent would not be applicable.

9. Similarly an extractor which depends upon the upward travel of tung kernels against the downward flow of solvent would not operate correctly since the solvent is denser than the oil being extracted. As the oil is removed by the solvent, the oil-solvent solution becomes less dense and the tendency of this solution is to rise rather than settle.

VI. SUMMARY

Tung oil, an important drying oil, is used in considerable amounts by the paint and varnish, linoleum, and electrical industries. At present domestic tung oil is obtained by mechanical expression. The cake which remains after expression has an oil content of from four to five per cent. Although the amount of domestic oil produced is a small part of the oil consumed in this country, tung oil shipments from China have ceased and the treatment of present and future domestic tung nut crops to obtain the maximum amount of oil most economically is a problem of considerable importance.

Solvent extraction has proven more efficient and economical in industries such as soybean and cottonseed oil extraction. It appeared feasible that tung oil might be extracted by analogous methods thus decreasing the loss of oil in the cake and increasing the efficiency and economy of tung oil production in the United States.

First Soxhlet extractions of ground tung kernels were performed with ethyl alcohol, benzene, carbon tetrachloride, chloroform, hexane, and toluene. Of the flammable solvents, benzene extracted the most oil, 51.7 per cent. Hexane was next in oil extraction with 50.8 per cent. In the non-inflammable class, carbon tetrachloride extracted the most oil, 47.8 per cent.

The compositions of non-inflammable mixtures of carbon tetrachloride with hexane and benzene were determined in a Cleveland open cup tester. A non-inflammable mixture of carbon tetrachloride - benzene (70 per cent and 30 per cent by volume respectively) was more economical than either a non-inflammable carbon tetrachloride - hexane mixture or carbon tetrachloride used alone. Consequently the carbon tetrachloride - benzene mixture was selected as the solvent to use in continuing the investigation.

Higher extraction efficiencies were obtained for batch extractions at 22 deg. C. with raw tung kernels than with roasted tung kernels. The highest extraction efficiency was obtained with raw tung kernels at 40 deg. C. for a batch extraction of 90 minutes.

Since the efficiencies of batch extraction are limited, preliminary investigations of the feasibility of using countercurrent extractors were made. These studies showed that the Allis-Chalmers and Ford type extractors were not applicable to the extraction of tung kernels with the carbon tetrachloride - benzene mixture since the tung kernels, as prepared, floated in the solvent mixture. The Allis-Chalmers extractor which depends upon the downward flow of the material being extracted against the upward flow of solvent would therefore not be suitable. Similarly the Ford type extractor would not be applicable because the solvent would have to travel

downward against the natural tendency of the oil being extracted and the oil-solvent solution formed to flow upward since they would be lighter than the original solvent mixture.

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APPENDIX

A. Selection of Non-Inflammable Solvent Mixture

1. Summary

Based upon the assumption that the solvent requirements and losses in tung oil extraction would be approximately the same as in soybean oil extraction, the following relationships were obtained. If the solvent requirements and losses for tung oil extraction be greater or less than those used here for soybean oil extraction, the costs of the two solvent mixtures relative to each other would vary correspondingly.

Basis: 1 ton of tung kernels to be extracted

a) Extraction with carbon tetrachloride alone.

Initial cost of solvent mixture -- $ 172.20

Cost of solvent lost ---------- $ 1.20

b) Extraction with 85 per cent carbon tetrachloride-15 per cent hexane (by volume)

Initial cost of solvent mixture -- $ 151.00

Cost of solvent lost ---------- $ 1.14

c) Extraction with 70 per cent carbon tetrachloride-30 per cent benzene (by volume)

Initial cost of solvent mixture -- $ 130.89

Cost of solvent lost ---------- $ 1.06

Note: Additional steam cost for the carbon tetrachloride-benzene mixture was negligible being only $0.01 more than the carbon tetrachloride - hexane mixture per ton of tung kernels treated.

On the basis of the above figures, a 70 per cent carbon tetrachloride - 30 per cent benzene mixture (by volume) was the one selected for further experimentation.

2. Calculations

The choice was between a carbon tetrachloride - hexane and a carbon tetrachloride - benzene mixture.

The percentages of oil removed from the original tung kernel samples as bases were as follows for the three solvents:

Carbon Tetrachloride ---------- 47.8

Hexane ---------- 50.8

Benzene ---------- 51.7

The amounts of oil removed by benzene and hexane were so nearly alike that these two solvents may be considered to be equally efficient in the removal of tung oil.

The prices of the three chemicals, from an inspection of the cost curve from 1919 to 1942, curves 6, 7, and 8, were:

Carbon Tetrachloride -------- $ 0.06 per pound

Hexane ---------- $ 0.10 per gallon

Benzene(90 per cent) -------- $ 0.16 per gallon

The densities of these three chemicals determined experimentally at 26 deg. C. were as follows:

Carbon Tetrachloride -------- 1.587 gm. per ml.

Hexane ---------- 0.663 gm. per ml.

Benzene ---------- 0.872 gm. per ml.

Therefore, at 26 deg. C., one gallon of hexane weighs 5.54 pounds and one gallon of benzene weighs 7.29 pounds.

Thus the costs of the chemicals may be retabuleted as follows: (The assumption was made that benzene, 90 per cent, had the same density as the benzene used in the laboratory.)

Chemical	Cost Per Gallon dollars	Cost Per Pound dollars
Carbon Tetrachloride	-----	0.06
Hexane	0.105	0.019
Benzene	0.16	0.022

The non-inflammable mixtures determined experimentally were as follows:

Mixture	Volume Basis		Weight Basis		Density at 26 deg. C. gm./ml.
	Flammable per cent	Carbon Tetrachloride per cent	Flammable per cent	Carbon Tetrachloride per cent	
Carbon Tetrachloride-Hexane	15.0	85.0	6.9	93.1	1.468
Carbon Tetrachloride-Benzene	30.0	70.0	19.0	81.0	1.371

Basis: 100 pounds of carbon tetrachloride - benzene non-inflammable mixture

Since volume and not weight is the important factor in extraction, the pounds of non-inflammable carbon tetrachloride-hexane

mixture equivalent to this basis are:

$$100 \times \frac{1.468}{1.371} = 107 \text{ pounds}$$

Costs of Non-Inflammable Mixtures.

Mixture	Weight of Flammable pounds	Weight of Carbon Tetrachloride pounds	Cost of Flammable dollars	Cost of Tetrachloride dollars	Total Cost of Mixture dollars
107 lb. of Carbon Tetrachloride - Hexane	7.4	99.6	0.141	5.976	6.117
100 lb. of Carbon Tetrachloride-Benzene	19.0	81.0	0.418	4.860	5.278

The following data taken from Lange[22] refer in all cases to the pure compound:

Compound	Latent Heat of Vaporization gm.cal./gm.	Specific Heat (Averaged Value) gm.cal./gm.-deg.C.	Boiling Point deg. C.
Carbon Tetrachloride	46.4	0.2	76.8
Hexane	79.3	0.6	69.0
Benzene	94.3	0.44	79.6

In the calculation of heat requirements the following assumptions were made:

a) Each solvent in the mixtures was vaporized at its individual boiling point.

b) Latent heats of vaporization and specific heats of the individual solvents in the mixtures were the same as they would be if present alone.

Therefore, based upon these assumptions,

a) the B.t.u. necessary to heat 1 pound of a 93.1 per cent carbon tetrachloride - 6.9 per cent hexane mixture (by weight) from 20 deg. C. to 76.8 deg. C. were 110.2.

b) the B.t.u. necessary to heat 1 pound of a 81.0 per cent carbon tetrachloride - 19.0 per cent benzene mixture (by weight) from 20 deg. C. to 79.6 deg. C. were 129.2.

In soybean oil extraction with hexane, the solvent losses amount to from 0.5 to 1.0 per cent of the weight of raw materials processed.(3) The solvent to bean ratio is 0.6 pounds of solvent per pound of bean. If the assumption be made that the solvent losses and the solvent to kernel ratio will be the same for tung oil extraction (using the higher figures in each case), the following relationships will hold:

Extraction With Carbon Tetrachloride Alone.

Basis: 1 ton of tung kernels to be extracted

Solvent Required = $0.6 \times 2000 \times \frac{1.58'}{0.663}$ = 2870 lb.

Solvent Lost = 0.01 x 2000 = ---------- 20 lb.

Initial Cost = 2870 x 0.06 = ... $ 172.20

Loss of Solvent = 20 x 0.06 = ... $ 1.20

Extraction With Carbon Tetrachloride - Hexane Mixture.

Basis: 1 ton of tung kernels to be extracted

Solvent required = $0.6 \times 2000 \times \frac{1.468}{0.663}$ = 2650 lb.

Solvent Lost = 0.01×2000 = ... 20 lb.

Initial Cost = $2650 \times \frac{6.117}{107}$ = ... $ 151.00

Loss of Solvent = $20 \times \frac{6.117}{107}$ = ... $ 1.14

Extraction With Carbon Tetrachloride - Benzene Mixture.

Basis: 1 ton of tung kernels to be extracted

Solvent Required = $0.6 \times 2000 \times \frac{1.371}{0.663}$ = 2480 lb.

Solvent Lost = 0.01×2000 = ... 20 lb.

Initial Cost = $2480 \times \frac{5.278}{100}$ = ... $ 130.89

Loss of Solvent = $20 \times \frac{5.278}{100}$ = ... $ 1.06

Heat Requirements.

Basis: 1 ton of tung kernels to be extracted

Heat Required For Vaporizing Carbon Tetrachloride-Hexane Mixture = 2650×110.2 = 292,000 B.t.u.

Heat Required For Vaporizing Carbon Tetrachloride-Benzene Mixture = 2480×129.2 = 320,500 B.t.u.

Additional Heat Required For Vaporizing Carbon Tetrachloride-Benzene Mixture = ... 28,500 B.t.u.

On the basis of $ 0.35 per 1000 lb. of steam, the additional steam cost for recovering the carbon tetrachloride-benzene mixture would be:

$$\frac{28,500 \times 0.35}{970 \times 1000} = \$\ 0.0103$$

B. Method of Calculation

Extraction Yields (Tables I to VII inclusive). Since the method of calculation for the extraction yields were the same for samples 1 to 28 inclusive, one calculation will suffice. For example, for sample 10 (Table III), the calculations involved were as follows:

Yield of oil = ... 27.53 gm.

Weight of sample = ... 52.53 gm.

Oil Removed-Basis:
Original Sample = $\frac{27.53}{52.53} \times 100$ = 52.4 per cent

Densities of Carbon Tetrachloride - Benzene Mixtures at 26 deg. C. (Table X). For example, the solution having a density of 1.089 consisted of 15.5 ml. of carbon tetrachloride and 34.8 ml. of benzene. Therefore, the composition of the mixture was:

Carbon Tetrachloride = $\frac{15.5}{15.5 + 34.8} \times 100$ = 30.8 per cent (by volume)

$$\text{Benzene} = \frac{34.8}{15.5 + 34.8} \times 100 = \ldots\ldots\ldots\ldots 69.2 \text{ per cent (by volume)}$$

Relationships between Percentages by Volume and by Weight of Carbon Tetrachloride - Benzene Mixtures (Table XI).

Let c = the volume fraction of carbon tetrachloride

b = the volume fraction of benzene

Density of carbon tetrachloride at 26 deg. C. = 1.587 gm./ml.

Density of benzene at 26 deg. C. = ... 0.872 gm./ml.

$$\text{Weight Per Cent Carbon Tetrachloride In Mixture} = \frac{c(1.587)}{c(1.587) + b(0.872)} \times 100$$

Also, $b = 1 - c$

Therefore, by simultaneous solution of the two equations,

$$\text{Weight Per Cent Carbon Tetrachloride In Mixture} = \frac{100}{\frac{0.549}{c} + 0.451}$$

Similarly,

$$\text{Weight Per Cent Benzene In Mixture} = \frac{100}{\frac{1.82}{b} - 0.82}$$

(Also the weight per cent benzene in the mixture = 100 minus the weight per cent of carbon tetrachloride in the mixture.)

The solution of composition 30.8 per cent carbon tetrachloride and 69.2 per cent benzene by volume was equivalent to a solution of composition:

$$\text{Carbon Tetrachloride} = \frac{100}{\frac{0.549}{0.308} + 0.451} = 44.8 \text{ per cent (by weight)}$$

$$\text{Benzene} = \frac{100}{\frac{1.82}{0.692} - 0.82} = 55.2 \text{ per cent (by weight)}$$

Addition of Solvents to Various Mixtures to Give a Solution Having a Composition 70 per cent Carbon Tetrachloride - 30 per cent Benzene by Volume at 26 deg. C. (Table XII).

Case 1 (Solutions having densities less than 1.371)

Let b = ml. of benzene present per 100 ml. of solution

c = ml. of carbon tetrachloride present per 100 ml. of solution

X_c = ml. of carbon tetrachloride to be added to give the correct final solution

But, $\frac{c + X_c}{b} = \frac{7}{3}$ and $b + c = 100$

Therefore, by simultaneous solution of the two equations,

$$X_c = \frac{10}{3}(70 - c)$$

For example, the solution having a density of 1.089 consisted of 30.8 per cent carbon tetrachloride by volume. Therefore,

$$X_c = \frac{10}{3}(70 - 30.8) = 130.7 \text{ ml. of carbon tetrachloride to be added}$$

Case 2 (Solutions having densities greater than 1.371)

Let b = ml. of benzene present per 100 ml. of solution

c = ml. of carbon tetrachloride present per 100 ml. of solution

X_b = ml. of benzene to be added to give the correct final solution

$$\text{But, } \frac{b + X_b}{c} = \frac{3}{7} \qquad \text{and } b + c = 100$$

Therefore, by simultaneous solution of the two equations,

$$X_b = \frac{10(30 - b)}{7}$$

For example, the solution having a density of 1.515 consisted of 9.9 per cent benzene by volume. Therefore,

$$X_b = \frac{10(30 - 9.9)}{7} = 28.7 \text{ ml. of benzene to be added}$$

Retention of Mixtures of Tung Oil and Solvent by Oil-Free Meal (Table XIII). For the solution of concentration 0.1000 gm. of oil per gm. of solution, the following calculations were involved:

Solution retained by b gm. of oil-free meal and thimble ..... 14.43 gm.

Solution retained by thimble ..... 3.07 gm.

Solution retained by b gm. of meal alone ..... 11.36 gm.

Therefore, solution retained per gm. of oil-free meal $= \frac{11.36}{5} = 2.27$ gm.

Roasting of Tung Kernels (Table XIV).

Original weight of kernels ..... 206.8 gm.

Loss in weight of kernels upon roasting ..... 6.5 gm.

Loss in weight of original sample $= \frac{6.5}{206.8} \times 100 = 3.14$ per cent

Moisture Content of Tung Kernels (Table XV). For sample 30, the following data were obtained:

Weight of kernels before drying ..... 20.282 gm.

Loss in weight of kernels upon drying ..... 0.568 gm.

Moisture present in original sample = $\frac{0.568}{20.282} \times 100 = 2.81$ per cent

Batch Extraction of Raw Tung Kernels (Tables XVI to XVIII).

Oil content of tung kernels ..... 51.3 per cent

Oil in 30 gm. of kernels = 30 x 0.513 = ... 15.39 gm.

Volume of solvent used ..... 175 ml.

Density of solvent at 26 deg. C. ..... 1.371 gm./ml.

Weight of solvent used = 175 x 1.371 = ... 240 gm.

If all the oil were extracted from the kernels by the solvent, the concentration of the final oil-solvent solution would then be:

$$\frac{15.39}{15.39 + 240} = 0.0603 \text{ gm. oil per gm. solution}$$

This theoretical maximum concentration applies to samples 32 to 43 inclusive. Since the method of calculation for all of these samples was the same, the following calculation for sample 41 (Table XVIII) was typical:

Final Concentration = 0.0508 gm. oil per gm. solution

Efficiency of extraction = $\frac{0.0508}{0.0603} \times 100 = 84.3$ per cent

Batch Extraction of Roasted Tung Kernels (Table XIX).

Since the raw tung kernels lost 3.14 per cent of their weight upon roasting, a 30 gm. sample of roasted tung kernels was equivalent to:

$$\frac{30}{1 - 0.00314} = 30.97 \text{ gm. of raw tung kernels}$$

Oil in 30.97 gm. of kernels = 30.97 x 0.513 = ... 15.89 gm.

Weight of solvent used ..... 240 gm.

If all the oil were extracted from the kernels by the solvent, the concentration of the final oil-solvent solution would then be:

$$\frac{15.89}{15.89 + 240} = 0.0621 \text{ gm. oil per gm. solution}$$

The calculation for sample 46 which follows was typical of those required for Table XIX.

Final concentration = 0.0507 gm. oil per gm. solution

$$\text{Efficiency of extraction} = \frac{0.0507}{0.0621} = 81.6 \text{ per cent}$$

C. Countercurrent Extraction Relations

For the special case in which the retention of solution per unit weight of solute-free inert solid is uniform with changing concentrations of solvent-oil solution, the following simplified method of calculation is applicable.

Since the retention of solutions having varying concentrations of tung oil and 70 per cent carbon tetrachloride-30 per cent benzene may be considered to be constant because of the nature of the data that was obtained, the method has been adapted specifically to the extraction of tung oil by this mixed solvent. In the discussion to follow, the word "solvent" will refer to this binary non-inflammable mixture.

Assumptions. The assumptions involved in this discussion are as follows:

1. Equilibrium is attained in every stage, which implies that the concentration of the solution retained by the solid is identical with that of the solution withdrawn.

2. Tung oil is not absorbed by oil-free tung meal.

3. The entering solvent contains no tung oil.

Let,

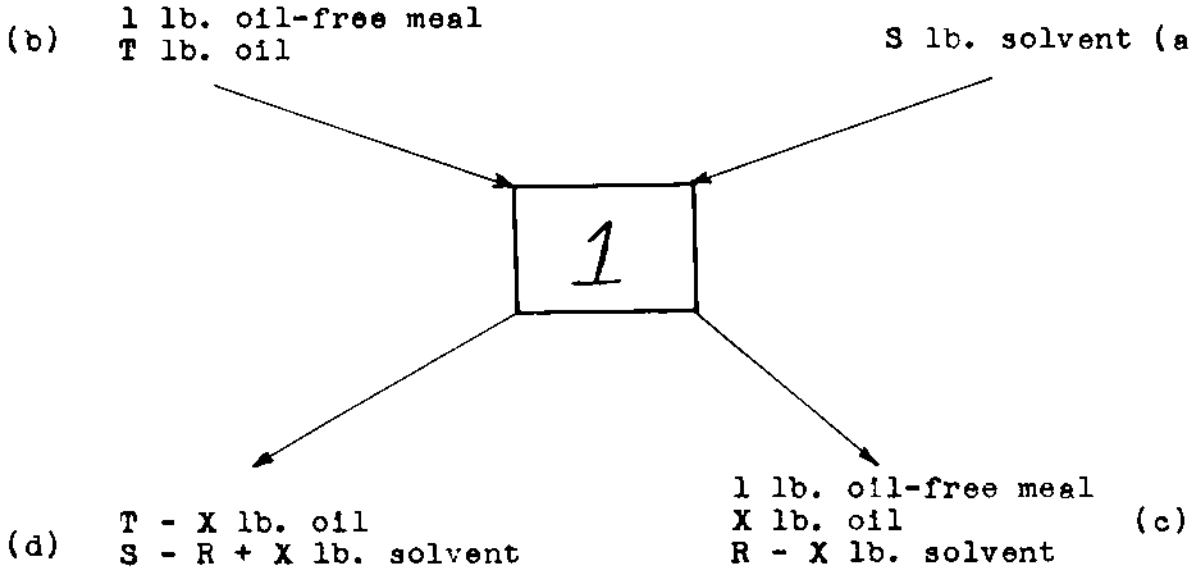
T = lb. of oil per lb. of oil-free tung meal entering the system at the first stage

R = lb. of oil-solvent solution retained per lb. of oil-free tung meal.

S = lb. of solvent added at last stage

X = lb. of oil discharged from last stage per lb. of oil-free tung meal

Case 1 --- One extraction stage



(a) is given
(b) is given
(c) .....Since X lb. oil are discharged and the total retention is R lb., then R - X lb. of solvent must be discharged.

(d) .....By a material balance,

Weight solvent = S - (R - X) = S - R + X lb.

Weight oil = T - X lb.

For equilibrium to have been established (assumption 1), the concentration of solution (d) must equal that of (c). Therefore,

$$\frac{T - X}{T - X + S - R + X} = \frac{X}{R - X + X}$$

$$\frac{T - X}{S - R + T} = \frac{X}{R}$$

$$\text{and } X = \frac{RT}{T + S}$$

Case 2 --- Two extraction stages (Figure 7)

(a), (b), (c), and (d) were obtained as in case 1.

(e).....Since the solution going from unit 1 to unit 2 and the strong solution being removed from unit 1 are in equilibrium, their concentrations are equal and therefore the oil going from stage 1 to stage 2 is:

$$\frac{(T - X)R}{T - X + S - R + X} = \frac{(T - X)R}{S - R + T}$$

Therefore, the weight of solvent is

$$R - \frac{(T - X)R}{S - R + T} \text{ lb. solvent}$$

(f) .....By a material balance over unit 2,

$$\text{Weight oil} = \frac{(T - X)R}{S - R + T} - X \text{ lb. oil}$$

$$\text{Weight solvent} = R - \frac{(T - X)R}{S - R + T} + S - (R - X)$$

$$\text{or Weight solvent} = S + X - \frac{(T - X)R}{S - R + T} \text{ lb. solvent}$$

For equilibrium,

$$\frac{\frac{(T - X)R}{S - R + T} - X}{\frac{(T - X)R}{S - R + T} - X + S + X - \frac{(T - X)R}{S - R + T}} = \frac{X}{R - X + X}$$

$$\text{or, } X = \frac{TR^2}{TR + S^2 + ST}$$

A relationship is more evident by solving for 1/X rather than X. For one unit,

$$\frac{1}{X_1} = \frac{1}{R} + \frac{S}{RT}$$

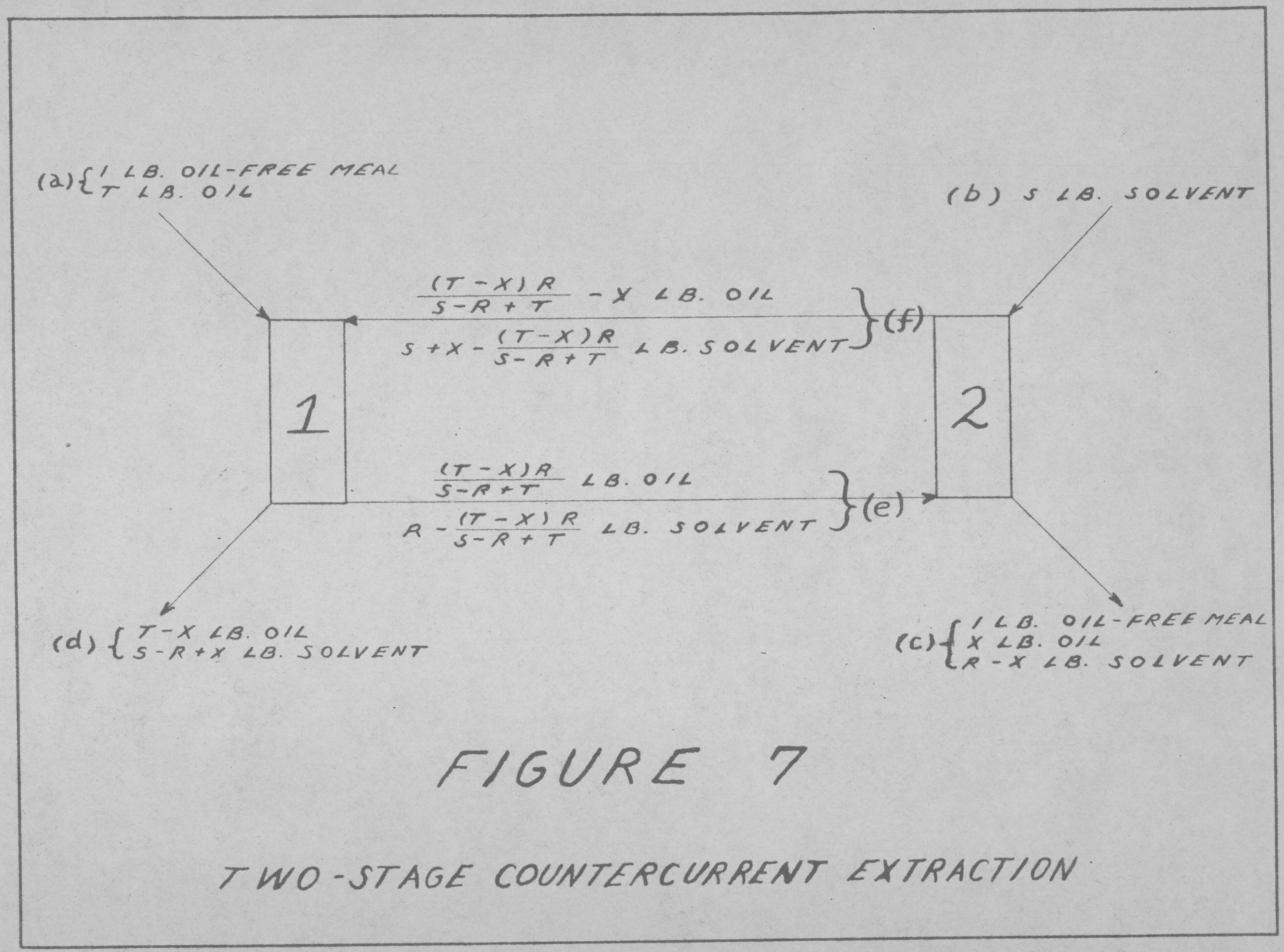


FIGURE 7

TWO-STAGE COUNTERCURRENT EXTRACTION

For two stages,

$$\frac{1}{X_2} = \frac{1}{R} + \frac{S}{R^2} + \frac{S^2}{R^2T}$$

By a continuation of this process, a relationship was found for X_n, the lb. of oil discharged from the nth stage per lb. of oil-free tung meal. This is as follows:

For $n \neq 1$

$$\frac{1}{X_n} = \frac{1}{R} + \frac{S^n}{R^nT} + \frac{S^{n-1}}{R^n} + \frac{S^{n-2}}{R^{n-1}} + \ldots\ldots\ldots\ldots + \frac{S}{R^2}$$

For $n = 1$

$$\frac{1}{X_1} = \frac{1}{R} + \frac{S}{RT}$$

Notes:

A. Overflow from every stage but first equals S + at lb.

B. Per 1 lb. of oil-free tung meal, there are the following variables:

1. T, the lb. of oil added with the meal. (This depends upon the oil concentration of the nuts.

2. X_n, the loss of oil in the meal from the last stage.

3. S, the lb. of solvent added.

4. The concentration of the strong solution from the first stage. This is always:

$$\frac{T - X}{S - R + T} \times 100 \text{ per cent of oil in solution}$$

5. N, the number of stages

6. R, the retention

Usually in a given system, T, the lb. of oil added with the oil-free meal is fixed, and for the particular system, the retention, R, is also fixed. Therefore, there are four variables, items 2, 3, 4, and 5. If the values of any two of these variables are fixed, the other two are automatically fixed.

For the special case of extraction of ground tung kernels with a 70 per cent carbon tetrachloride - 30 per cent benzene mixture, R = 2.32. The oil content of the original tung kernels was 51.3 per cent. Therefore,

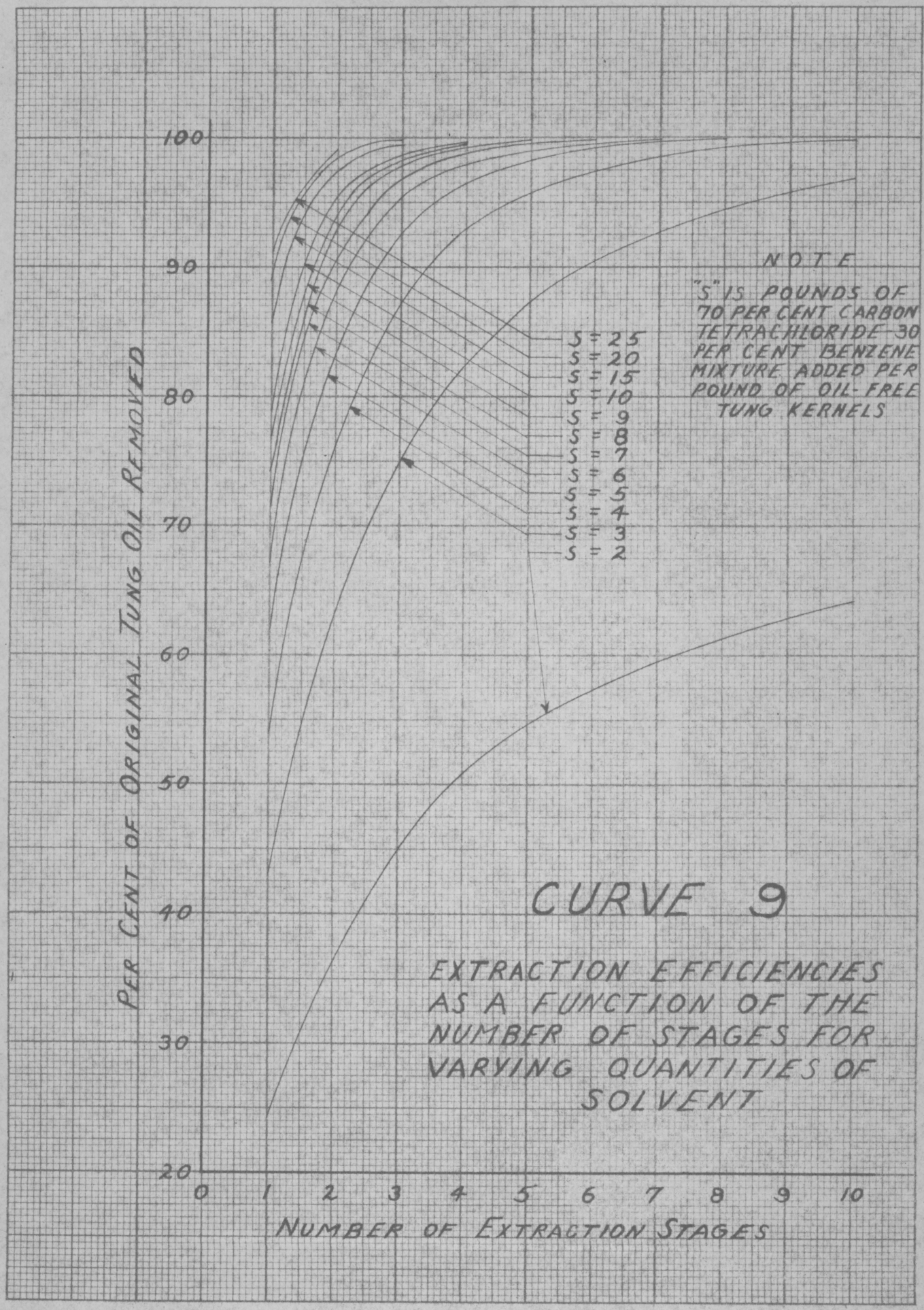
$$T = \frac{0.513}{0.487} = 1.053$$

Therefore, there will be three variables, S, X, and the number of stages. A plot of these is given in Curve 9, which has one minor change in it. Instead of representing X, the oil remaining in the meal, the per cent of oil removed is plotted as the ordinate.

Method of Preparing Curve. What is the per cent of original tung oil removed in a three-stage extractor when S equals 6?

For three stages,

$$\frac{1}{X_3} = \frac{1}{R} + \frac{S^3}{R^3 T} + \frac{S^2}{R^3} + \frac{S}{R^2}$$


100
90
80
70
60
50
40
30
20
0
1
2
3
4
5
6
7
8
9
10
PER CENT OF ORIGINAL TUNG OIL REMOVED
NUMBER OF EXTRACTION STAGES
S = 25
S = 20
S = 15
S = 10
S = 9
S = 8
S = 7
S = 6
S = 5
S = 4
S = 3
S = 2
NOTE
"S" IS POUNDS OF 70 PER CENT CARBON TETRACHLORIDE 30 PER CENT BENZENE MIXTURE ADDED PER POUND OF OIL-FREE TUNG KERNELS
CURVE 9
EXTRACTION EFFICIENCIES AS A FUNCTION OF THE NUMBER OF STAGES FOR VARYING QUANTITIES OF SOLVENT

$$T = 1.053$$

$$R = 2.32$$

$$S = 6$$

By substituting,

$$\frac{1}{X_3} = 20.84 \qquad X_3 = 0.0478$$

Since there was originally present 1.053 lb. oil, the oil removed was:

$$100 \times \frac{1.053 - 0.0478}{1.053} = 95.4 \text{ per cent}$$

Sample Problem. The use of Curve 9 in predicting theoretical extractions for one type of extraction problem for the particular tung kernel samples used in this thesis with the given mixed solvent is shown by the following:

A battery of four extractors are operating in such a way that fifty lb. of tung kernels are extracted per hour with 100 lb. of 70 per cent carbon tetrachloride - 30 per cent benzene. a) What percentage of the original tung oil may be removed? b) What is the weight of oil remaining in the meal?

a) Oil in 50 lb. kernels = 50 x 0.513 = 25.6 lb.

Oil-Free meal = 50 - 25.6 = ... 24.4 lb.

Solvent per lb. oil-free meal = $\frac{100}{24.4}$ = 4.10 lb.

From Cuve 9, for S = 4.10 and 4 units, the per cent oil removed = 93 per cent.

b) Oil remaining in meal = (1 - 0.93)(25.7)

= 1.8 lb.