

DESIGN CHARACTERISTICS FOR
BYPRODUCT FATTY ACID RECOVERY

by

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in

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PART I

INTRODUCTION

INTRODUCTION

In the manufacture of kraft paper pulp from pine wood the original fats and resins present in the wood are saponified by the action of the caustic cooking liquor during digestion of the pulp and pass off as soluble soaps in the waste liquor from the digesters.

After the pulp is washed free of waste liquor, the washings are combined with the original waste liquor and sent to the evaporators as the first steps in the recovery of the chemicals present. During the process of evaporation, as the black liquor becomes more and more concentrated the saponified fats and resins separate out. Due to this separation their presence causes real trouble in the evaporators for two reasons: viz.--the first is that the soaps cause a tremendous amount of foaming and the evaporators prime over, thus making operation difficult; second, the soaps cake and dry on the evaporator tubes, cutting down the coefficient of heat transfer, and necessitating frequent cleaning.

For years the resin soap has been removed at an intermediate stage in evaporation and then pumped to the furnaces where it is burned for its heat value. Beginning approximately in 1907 a considerable amount of research has been done on the material, particularly in Europe, both as to the identification of the constituents of the resin soaps and also as to their utilization.

A number of plants for the recovery of this material are in operation in Europe, but so far as is known, only one such plant is operating in the United States.

According to an editorial (11-a) the total sulphate and soda pulp

produced in the United States in 1935 was 1,415,096 tons. The estimated production for the year 1936 was 1,802,000 tons; and there are ten new kraft mills under construction in the Southern states which will add an estimated 1,225,000 tons capacity to the present capacity.

From the above it will be seen that a conservative estimate of the production for the year 1937 would be 2,000,000 tons.

According to Schmid (52) for each ton of pulp produced there are 30 kg. of fats and resins available or 3.3% by weight; Bergstrom and Cederquist (5-a) state that there are 32.5 kg. of fats and resins present in the wood used to make one ton of pulp, and that after cooking there is available 13.5 kg., or 1.5% by weight. Hilding (27) states that there is available in the wood 1.5% by weight of the fats and resins. From the evidence as above, the amount of fats and resins available can be conservatively estimated at 1.5% by weight for each ton of pulp produced. However, it must be remembered that these analyses were all made on the coniferous woods of Northern Europe, and we would expect a higher yield from the Southern pine. This assumption is borne out by the experience of the author in a kraft mill producing 350 tons of pulp per day; the average over a four-year period being approximately 2% by weight of the pulp produced. This percentage varied according to the greenness of the wood being cooked, the greenest wood giving the largest yield of sodium resinate. This fact was also reported by Cirves (25).

Thus for a total annual production of 2,000,000 tons of sulphate and soda pulp there would be available 40,000 tons of crude fatty acids on a conservative estimate. At the present time the only value that the material has is for fuel, at a value not exceeding \$6.00 per ton. By refining the material the value per ton can be increased to \$30.00 with conversion costs of approximately \$24.00 per ton, thus yielding to the

industry a net increase of \$5000 per ton or a total annual increase of \$2,000,000.

From the evidence it may be seen that the recovery of this byproduct is attractive to any kraft mill using Southern pine as a raw material.

The purpose of this investigation is to determine the distillation characteristics of the crude fatty acids from the sodium resinate and their corrosion characteristics in order that efficient units may be designed for the recovery of valuable products.

Nomenclature

Owing to the involved nomenclature which has developed in the past years it is deemed advisable to review briefly the various characterizations which have been used, and to clearly define the terms used in this investigation.

The saponified fats and resins that separate out from the waste or black liquor of the soda and sulphate pulp processes, have been called sodium resinate, sodium rosinate, liquid rosin, liquid resin, floating resin, raw sulphate resin, rosin soap. Sodium resinate is the term most frequently used in the U. S. and floating resin the most common in Europe. In this discussion sodium resinate will be used to denote the saponified fats and resins.

After the sodium resinate has been treated with a mineral acid to regenerate the fatty acids, the resulting oily, viscous liquid has been called liquid rosin, liquid resin, crude fatty acids tall oil, tallol, pinolein, Swedish rosin oil, and various trade names. Crude tall oil is the most widely accepted term in Europe and liquid rosin in the U. S. For the purpose of this discussion crude fatty acids has been selected as the term most clearly indicating the material.

For the first fraction from the distillation of the crude fatty acids all of the above mentioned terms have been used. In European practice distilled tall oil is the usually accepted term, and for our usage distilled fatty acids has been selected.

For the intermediate fraction that crystallizes from the distillate, the terms abietic acid, crystalline rosin, and rosin acids are generally used. This crystalline product has been identified by a number of investi-

gators as abietic acid, which term will be used in this investigation.

Pitch is the only name that has been given to the residue from the distillation.

Historical

In 1911 Hilding (27) formed crude fatty acids from the rosin soaps and reported that after distillation under reduced pressure an analysis (by Twitchell's method) of the distillate showed 53.1% fatty acids and 46.9% rosin acids. The distillate after being freed of crystals of rosin acids and distilled again showed oleic, palmitic and linolenic acids. Examination of the rosin acids after washing with petrol and recrystallization from alcohol showed the product was a mixture with a melting point of 166-180°, acid number 186.6 and dextrorotatory. He also reported that phytosterol may be extracted.

In 1919, Aschan and Eckholm (2) reported "pinabietic acid" present in the crude fatty acids, isolated as shining needles (m.p. 176°). They also reported that the specific rotation of the material depended upon the solvent used, the crystals being d-rotatory in aromatic hydrocarbons but l-rotatory in aliphatic hydrocarbons.

In 1921 Hubscher (31) reported the following analysis:

	Tall Oil	Tall Oil Distillate	Tall Oil Pitch
Specific Gravity	0.976	0.958	---
Acid Number	114	152	50.3
Saponification Number	129	162	75.5
Iodine Number	---	107	---
Melting Point	---	---	85°

The crystals obtained from the distillate, when twice recrystallized from alcohol showed a melting point of 170° and a saponification number of 195.6. Hubscher also stated that the crystals were considered to be pure abietic acid.

In 1926 Dittmer (14) reviewed previous investigations of rosin soaps (talloil) and upon analysis resolved it into the following fractions: petroleum ether insoluble, 2.2%; unsaponifiable 12.4%; "fatty acids" 54.9%; resin acids 30.4%. He identified oleic, linolenic and linolic acids by oxidation and bromination products and also concludes that the rosin acids consist of abietic acid only.

Keghel (34) in 1927 identified "talloleic", linolenic and lauric acids. Pyhala (46) also identified oleic, linolenic and ricinoleic and small amounts of erucic and palmitic acids. However, Hasselstrom (23) pointed out that the palmitic acid is probably produced from oleic acid by the cooking process.

From the agreement of the published data on crude and distilled fatty acids, and the entire lack of any contradictory evidence, it may safely be concluded that the composition of the divisions are as follows:

Crude fatty acids: principally oleic, with linolenic, linolic and small amounts of related acids.

Rosin acids: Abietic acid.

Pitch: Undetermined, but probably consisting principally of polymerization products.

At this point it would be advisable to state that the resin contents of the coniferous pulp wood of Europe ^{and} the Southern pine wood do not differ to any marked extent in their constitution but principally in the quantity present. This is confirmed in the literature and by comparison

of the physical and chemical characteristics of published results of European investigators with unpublished analyses by the author of crude fatty acids and distilled fatty acids from Southern pine pulp production.

In order to more clearly illustrate this similarity the following table has been prepared. The analyses on the crude and distilled fatty acids from Southern pine were made by the author and those on the European crude and distilled fatty acids were taken from the following references: Alberti (1); Hilding (27); Pyhala (46); de Keghel (34); Hubscher (31); Dittmer (14); Dittler (13).

	European Crude	Southern Crude	European Distilled	Southern Distilled
Acid Number	114	120-130	150-183	150-170
Saponification Value	129	120-130	150-185	150-170
Iodine Value			107-140	100-118
% Fatty Acids		17-25	45-55	43-50
% Rosin Acids		45-65	30-47	38-45
% Unsaponifiable (Sterols)		20-30	8-30	13-18

Refining of Crude Fatty Acids

In general the refining of crude fatty acids or any very high b. p. material by distillation is carried out at the highest possible vacuum and with steam to lower the vapor pressure of the desired product. The use of steam was necessary in the past since it was not economically possible to attain high vacuums, or more correctly, low absolute pressures, under plant conditions. However, recent industrial developments along this line now permit almost any desired absolute pressure to be attained in plant practice. As a natural result the use of steam for distillation of high boiling point materials is rapidly decreasing. Other contributing factors are the large amount of steam required over the theoretical amount due to the fact that the intimate mixing of the material to be distilled and of steam have proved impossible of attainment, thus necessitating the use of a large excess of steam. For very high boiling point materials steam becomes merely an efficient stirring device to prevent local overheating and acting as a carrier for the vapors, but not as the theory of steam distillation would have us believe.

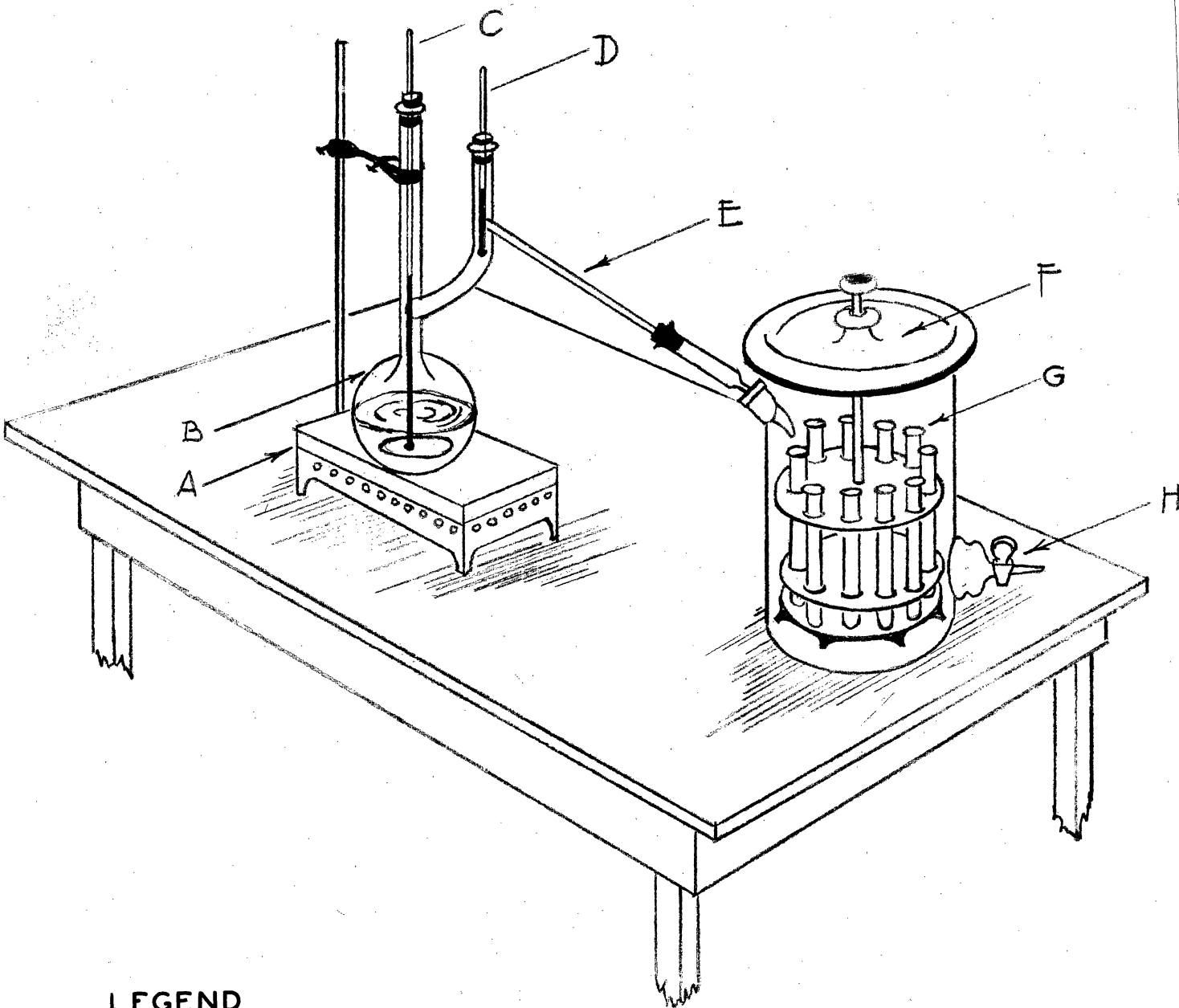
The most modern designs for the distillation of high boiling point materials have eliminated the use of steam altogether.

For the reasons as stated above the distillation work of this research was carried out at an absolute pressure of 5-7 mm. and without the use of steam in order to permit the use of the data obtained for the design of modern distillation units according to the best practice.

A search of the literature revealed no information whatever on the distillation characteristics of crude fatty acids from the production of paper pulp from Southern pine wood. It is hoped that the information

obtained from this investigation will furnish the basic information necessary for the proper design of byproduct recovery units.

DISTILLATION CHARACTERISTICS



LEGEND

- A ELECTRIC HEATER
- B DISTILLATION FLASK
- C THERMOMETER
- D THERMOMETER
- E ARM OF FLASK
- F DISTILLING RECEIVER
- G COLLECTION TUBES
- H VACUUM CONNECTION

DISTILLATION CHARACTERISTICS

Procedure

A five gallon sample of the crude fatty acids was used as the crude oil for distillations numbers 1, 2, and 3 for runs under 5-7 mm. absolute pressure respectively.

A sample of the crude fatty acids was weighed into a tared Claisen flask, stoppered with two rubber stoppers bearing A. S. T. M. Fahrenheit thermometers, one extending down into the oil and the other in the vapor outlet of the flask. The temperatures read on these thermometers are designated the oil temperature (T_o) and the vapor temperature (T_v), respectively. The flask was placed on an adjustable electric heater of 760 watts capacity. An adjustment to about 530 watts was found to give a good rate of distillation and so was made standard. The flask was completely lagged with asbestos rope. The arm of the flask was connected to a Pyrex distilling receiver, containing nine weighed tubes. Each of these tubes held approximately 30 c. c. and so in each case approximately 300 grams was weighed into the flask.

The connection to the vacuum line was made next and the vacuum turned on at the same time as the heat.

Approximately two hours was required for the first drop of distillate to come over; distillation was then completed in another hour. Three temperature readings were taken while each sampling tube was being filled, as near as possible for each 10 c. c. distilled.

After all of the tubes were filled with distillate, the heat was turned off, and the vacuum maintained until the tubes had cooled. This was done in order to prevent oxidation of the contents of the tubes and

the flask. The lagging was removed and the flask and its contents weighed.

The content of each tube was weighed and analyzed, after being thoroughly mixed to prevent possible erroneous results due to layering off in the tubes. No analysis was run on the pitch or residue since we know of no reliable methods of analyzing this substance. From the constants determined as above the fatty acid content, calculated as oleic acid, the content of rosin acid, calculated as abietic acid, and the unsaponifiable matter or sterols, calculated by difference, were made.

Tables and charts were prepared illustrating the results.

Data and Results

DISTILLATION A.

This was a preliminary distillation undertaken as a guide into the more complete research. It was performed before the Pyrex distilling receiver was available, and the results are rather brief.

The distillation was performed in exactly the same manner as the others, except that an ordinary vacuum flask was used in the place of the Pyrex receiver as shown on the sketch of the equipment. At two intervals during the course of the distillation the flask and its contents was weighed in order to determine what percentages were distilled at the specified temperature.

The comparatively large loss is probably due to the fact that the distillation was stopped at these intervals and consequently there was some vapor loss. Also the accuracy of the weighings is somewhat lower than the other distillations, since it was impossible to use an analytical balance on the flask.

DISTILLATION A

TABLE I--A

Distillation of Crude Fatty Acids at 5-7 mm. Absolute Pressure

Fraction	Temp. °Fv	Total gms.	Acid No.	Rosin Acid No.	Fatty Acids %	Abietic Acid %	Sterols (calc.) %	Recovery %
Distillate	435-490	360	155	117	19	63	18	81
Pitch		58						13
Losses, etc.		27						6
Crude		445	138	106	16	57	27	

DISTILLATION NO. I.

Gas began to evolve at 140°F_0 and continued until the boiling point was reached. This evolution was not violent but rather steady. The liquid began to boil steadily at 410°F_0 , but the temperature continued to rise until it reached 488°F_0 where it remained constant as the oil refluxed back into the flask. After the flask and lagging had been thoroughly warmed, this refluxing ceased and the distillate began to come over. Fumes became visible in the distilling receiver at a vapor temperature of 166°F_v .

In this distillation the arm of the flask was not lagged, and just after the fourth tube was filled the distillate froze in the arm of the flask, thus breaking the vacuum in the flask. As the frozen arm cleared, the sudden decrease in absolute pressure caused the flask to prime over and the distillation was stopped.

DISTILLATION NO. I

TABLE I

Distillation of Crude Fatty Acids at 5-7 mm. Absolute Pressure

Fraction	Temp. °Fv	Total gms.	Acid No.	Rosin Acid No.	Fatty Acids %	Abietic Acid %	Sterols (calc.) %	Recovery %
1.	444	29.3	124	41	42	22	36	
2.	449	30.1	163	71	46	38	16	
3.	460	31.2	171	92	40	50	10	
4.	477	32.9	175	120	28	65	7	
Crude		232	138	98	17	56	27	

Distillation incomplete due to freezing of distillate in the arm of the flask.

DISTILLATION NO. 2

The same characteristics were observed in this distillation as in No. 1, with the temperatures agreeing within one or two degrees. However, in this case, the arm of the flask was lagged and no difficulty was experienced with the distillate freezing. The distillation proceeded smoothly, with no unusual features until the ninth tube was being filled. The distillate had begun to darken slightly in filling tube eight, but when tube nine was about half full, the distillate darkened rapidly and quite a lot of gas began to evolve. After cooling, a distinct layer was apparent between the upper and the lower half of the tube. The two layers were easy to separate, the upper being much less viscous, and so it was thought best to analyze each of them separately, which was done. The upper half of the tube was called number 10 in the sampling series.

DISTILLATION NO. 2

TABLE II

Distillation of Crude Fatty Acids at 5-7 mm. Absolute Pressure

Fraction	Temp. °F _v	Total gms.	Acid No.	Rosin Acid No.	Fatty Acids %	Abietic Acid %	Sterols (calc.) %	Recovery %
1.	428	29.1	126	43	40	25	35	
2.	444	28.5	155	63	47	34	19	
3.	453	29.3	167	82	43	44	13	
4.	460	29.8	171	104	34	56	10	
5.	468	29.5	175	123	26	66	8	
6.	478	30.1	175	145	15	78	7	
7.	486	30.2	172	155	10	84	6	
8.	491	31.7	165	150	11	82	7	
9.	498	16.5	147	125	11	67	22	
10.	512	16.9	124	105	10	57	33	
Total Distillate:		271.6	--	--	25.8	59.6	14.6	82.3
Residue		54						16.4
Loss, etc.		4						1.3
Crude		330	135	104	17	56	27	

DISTILLATION NO. 3

Due to observations made during distillation No. 3, it was thought that there might be some definite point at which the fatty acids begin to decompose. In order to clarify this point a slightly different procedure was followed in this distillation. It was begun in the same manner except that the distillate was caught in a flask placed in the distilling receiver, until approximately 150 c. c., or half of the original sample was distilled off. The same characteristics were observed in this distillation as in the previous ones. After the flask had been filled, the distillation was stopped, the flask removed, and the sample tubes placed in the receiver. For the remainder of the run only 15 c. c. were caught in each tube and even less in the case of the last two tubes. Three temperature readings were taken as before, but this time they were for each c. c. instead of each 10 c. c. There was no layering off noted in the tubes, but at a vapor temperature of 490°F_v , the same as in distillation No. 2, there was considerable darkening of the color of the distillate and gas began to evolve increasing tremendously at 495°F_v . The residue in the flask was carbonized.

DISTILLATION NO. 3

TABLE III

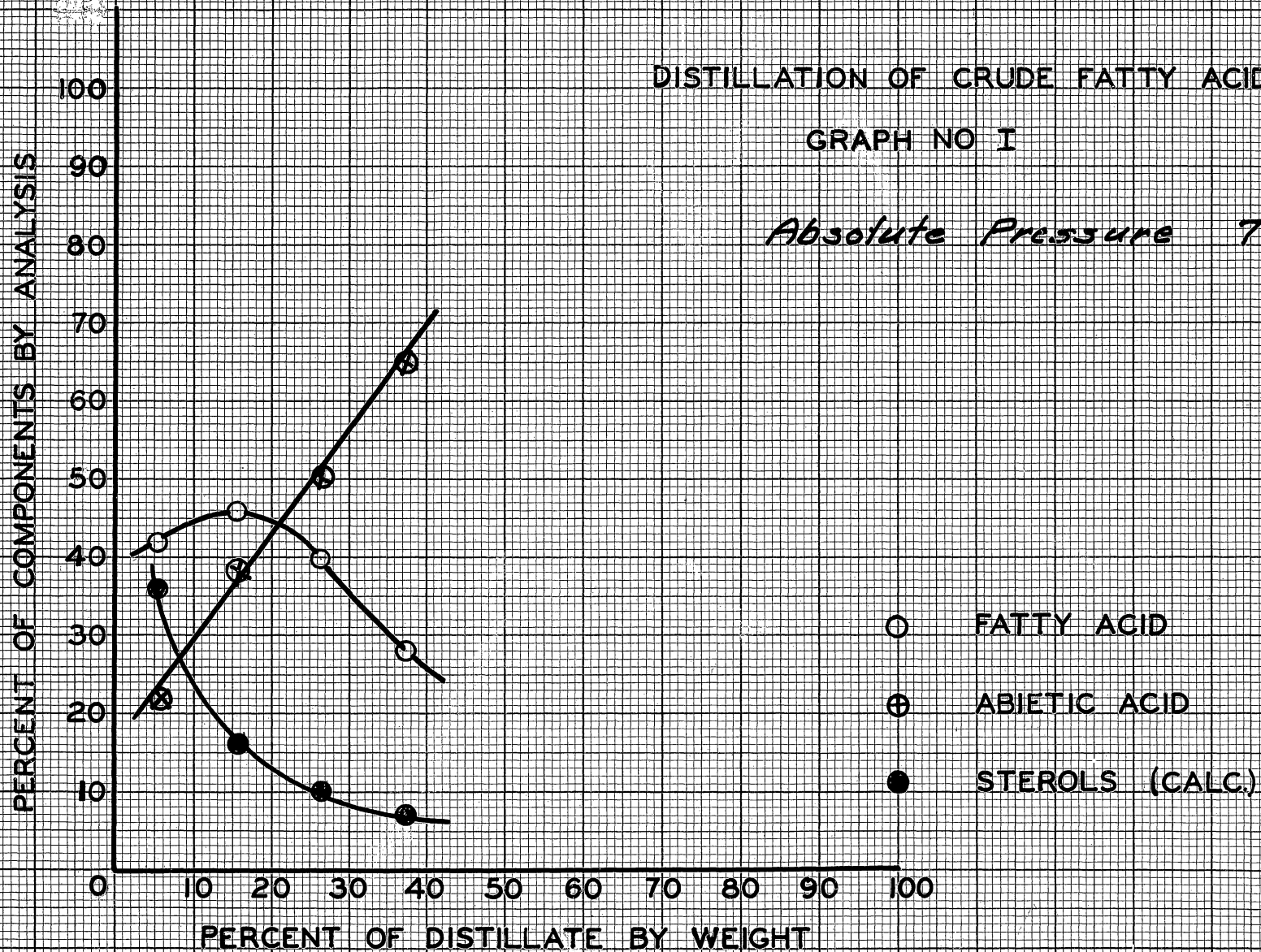
Distillation of Crude Fatty Acids at 5-7 mm. Absolute Pressure

Fraction	Temp. : °F _v	Total : gms.	Acid : No.	Rosin : Acid : No.	Fatty : Acids : %	Abietic : Acid : %	Sterols : (calc.) %	Recovery : %
1.	467	137.1	161	87	37	47	16	
2.	467	19.3	168	130	19	70	11	
5.	470	19.3	174	145	15	78	7	
4.	475	19.6	171	155	8	84	8	
5.	476	17.4	167	153	8	82	10	
6.	481	18.5	154	142	6	77	17	
7.	490	11.1	136	117	10	63	27	
8.	495	11.7	103	76	14	41	45	
9.	508	12.5	66	36	15	19	66	
10.	568	10.9	42	26	8	14	78	
Total Distillate:		277.4	--	--	24.2	55.4	20.4	90.8
Residue		30.0						9.9
Loss, etc.		0						0
Crude		306.0	135	103	17	56	27	

DISTILLATION OF CRUDE FATTY ACIDS

GRAPH NO I

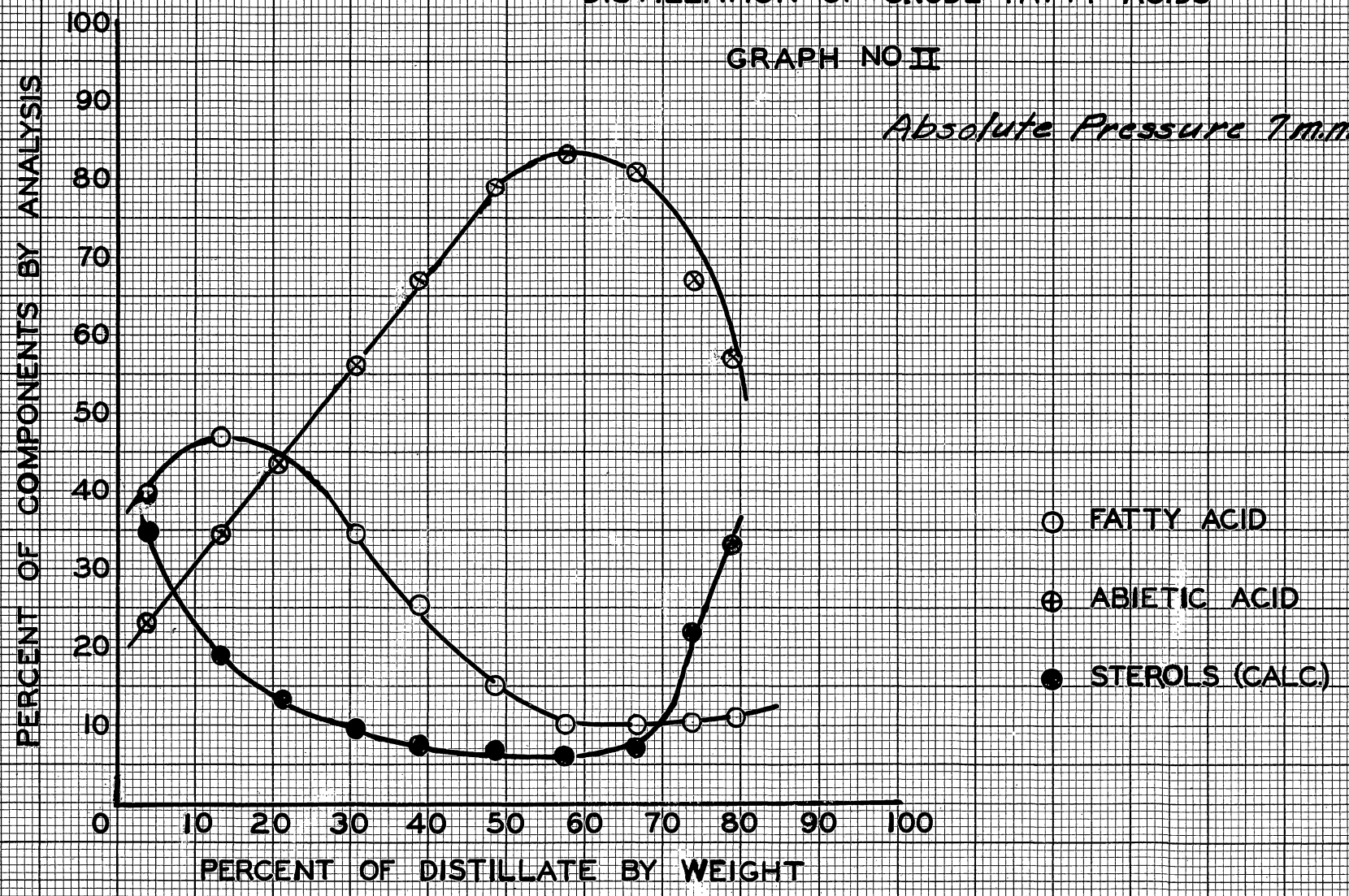
Absolute Pressure 7 m.m.



DISTILLATION OF CRUDE FATTY ACIDS

GRAPH NO II

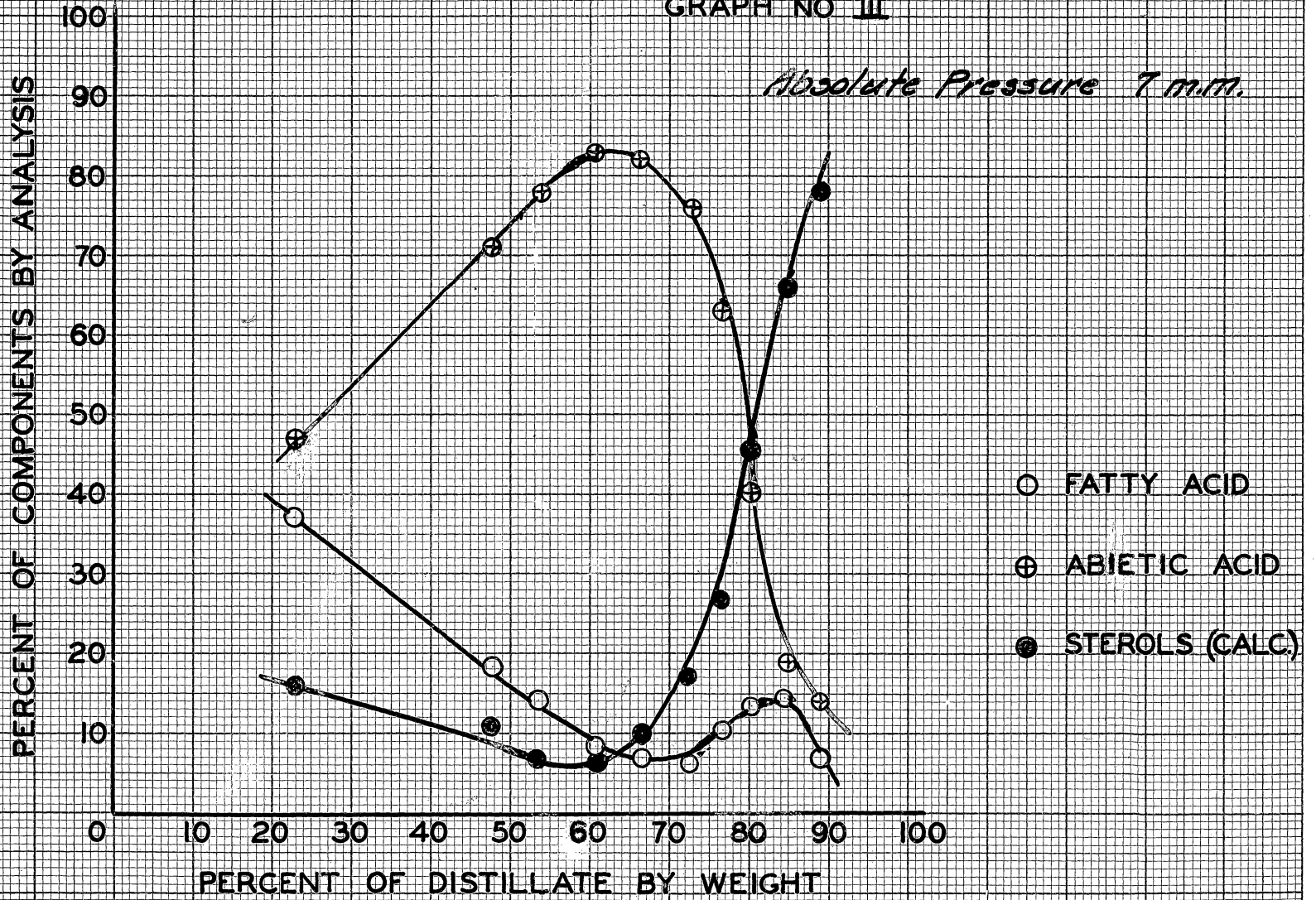
Absolute Pressure 7mm.

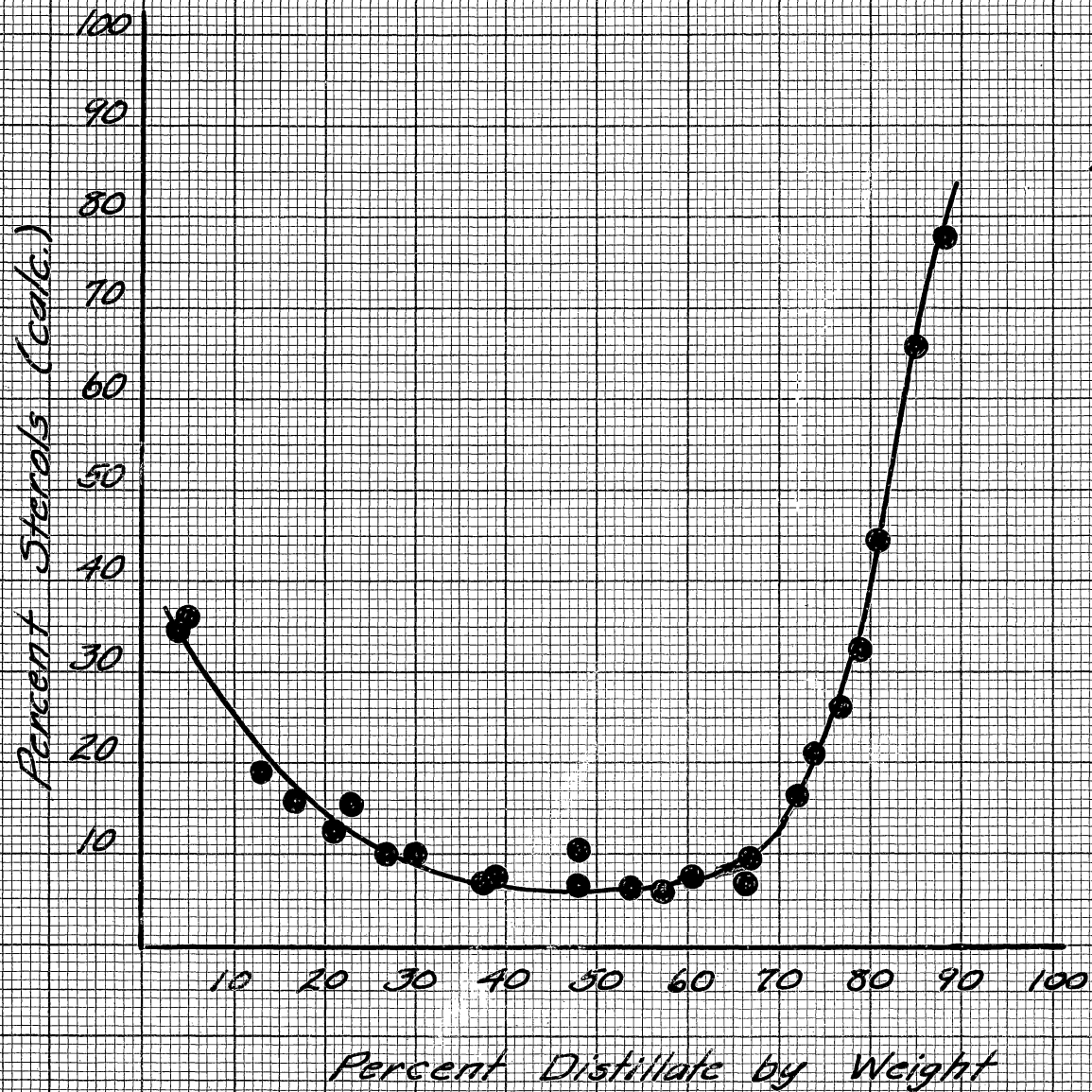


DISTILLATION OF CRUDE FATTY ACIDS

GRAPH NO. III

Absolute Pressure 7 m.m.

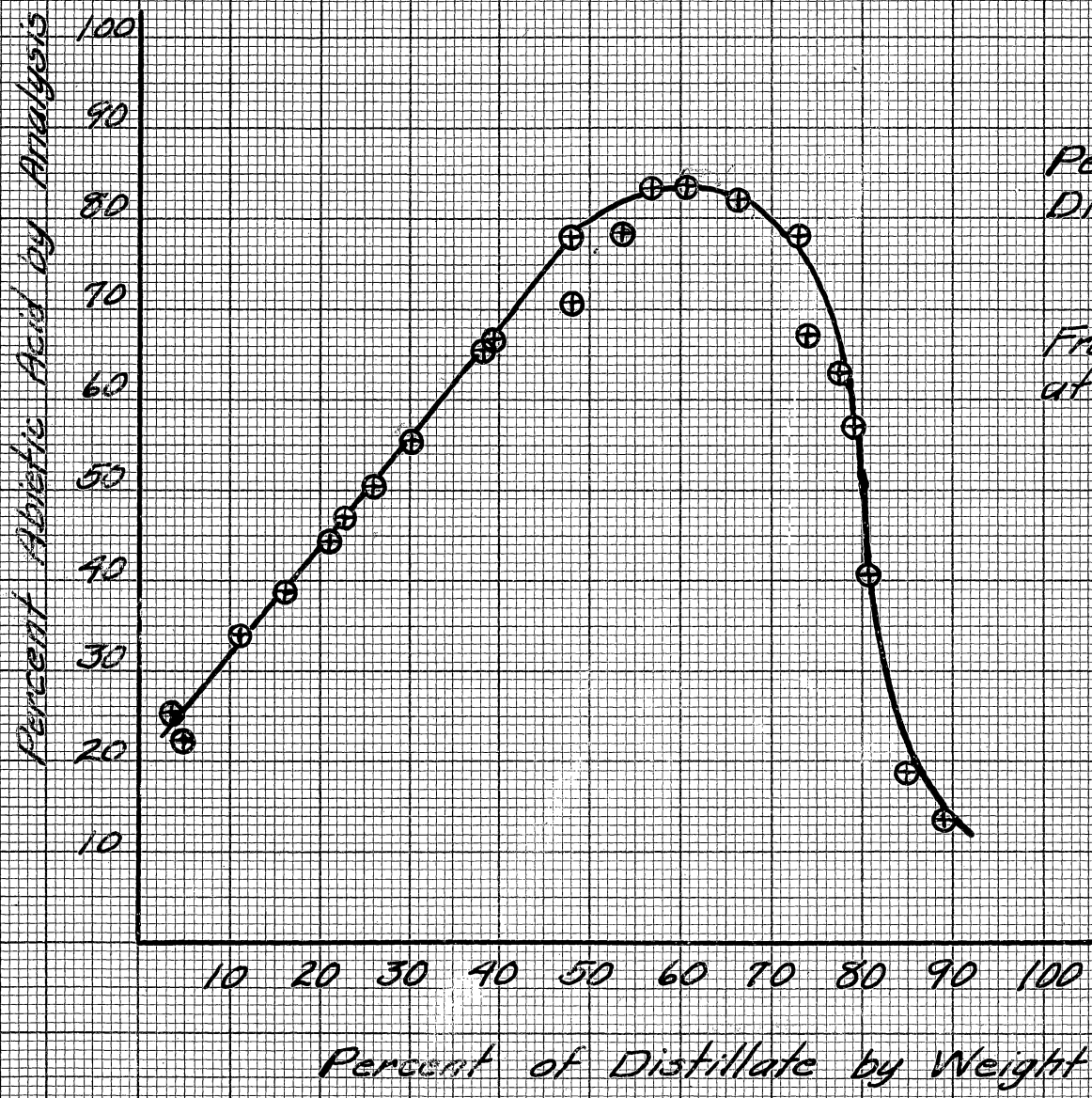




GRAPH IV.

Percentage of Sterols
in Distilled Fatty Acids

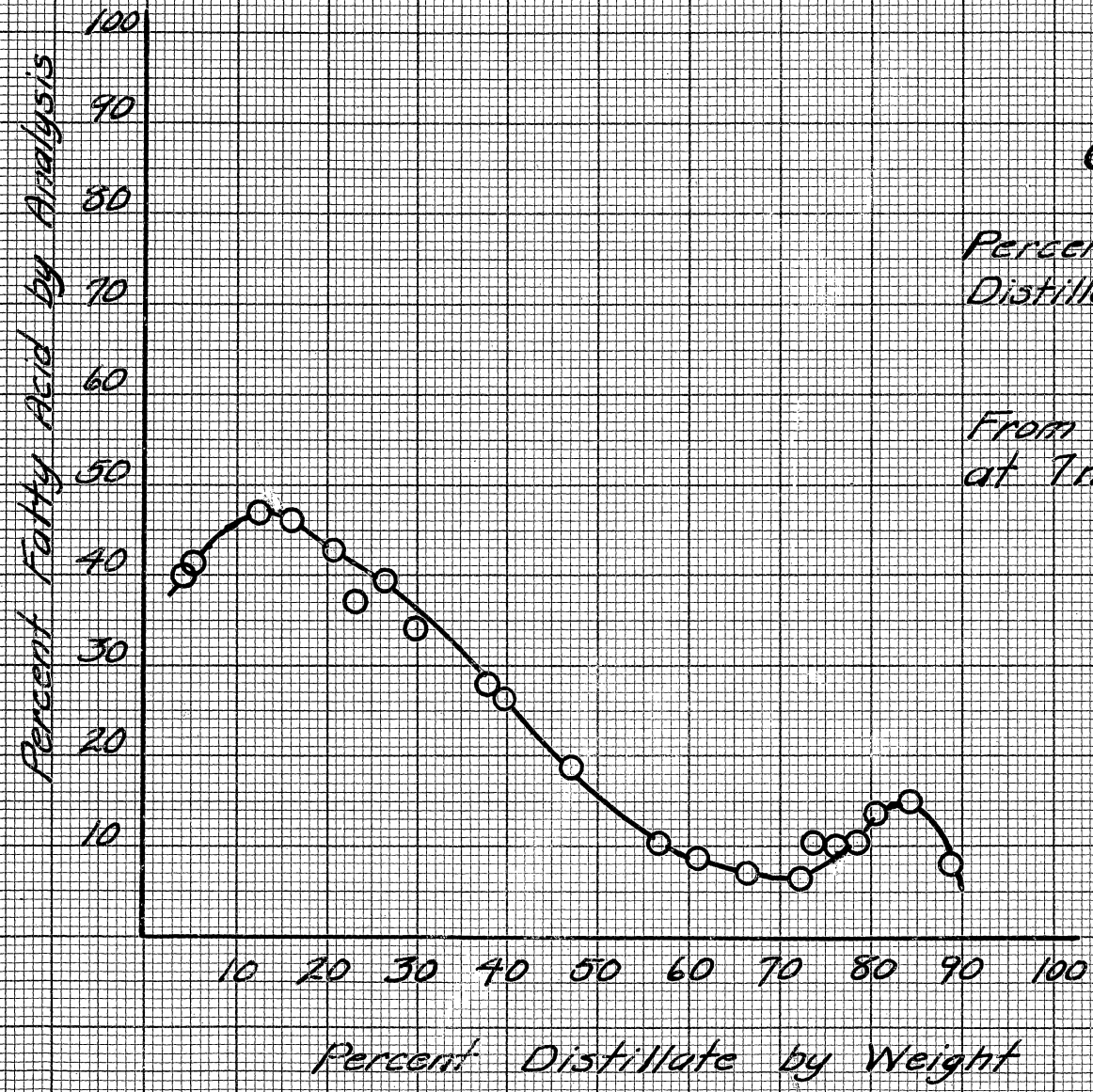
From Distillations 1, 2, + 3
at 7 m.m. Absolute Pressure



GRAPH V.

Percent Abietic Acid in Distilled Fatty Acids.

From Distillations 1, 2, + 3. at 7 m.m. Absolute Pressure



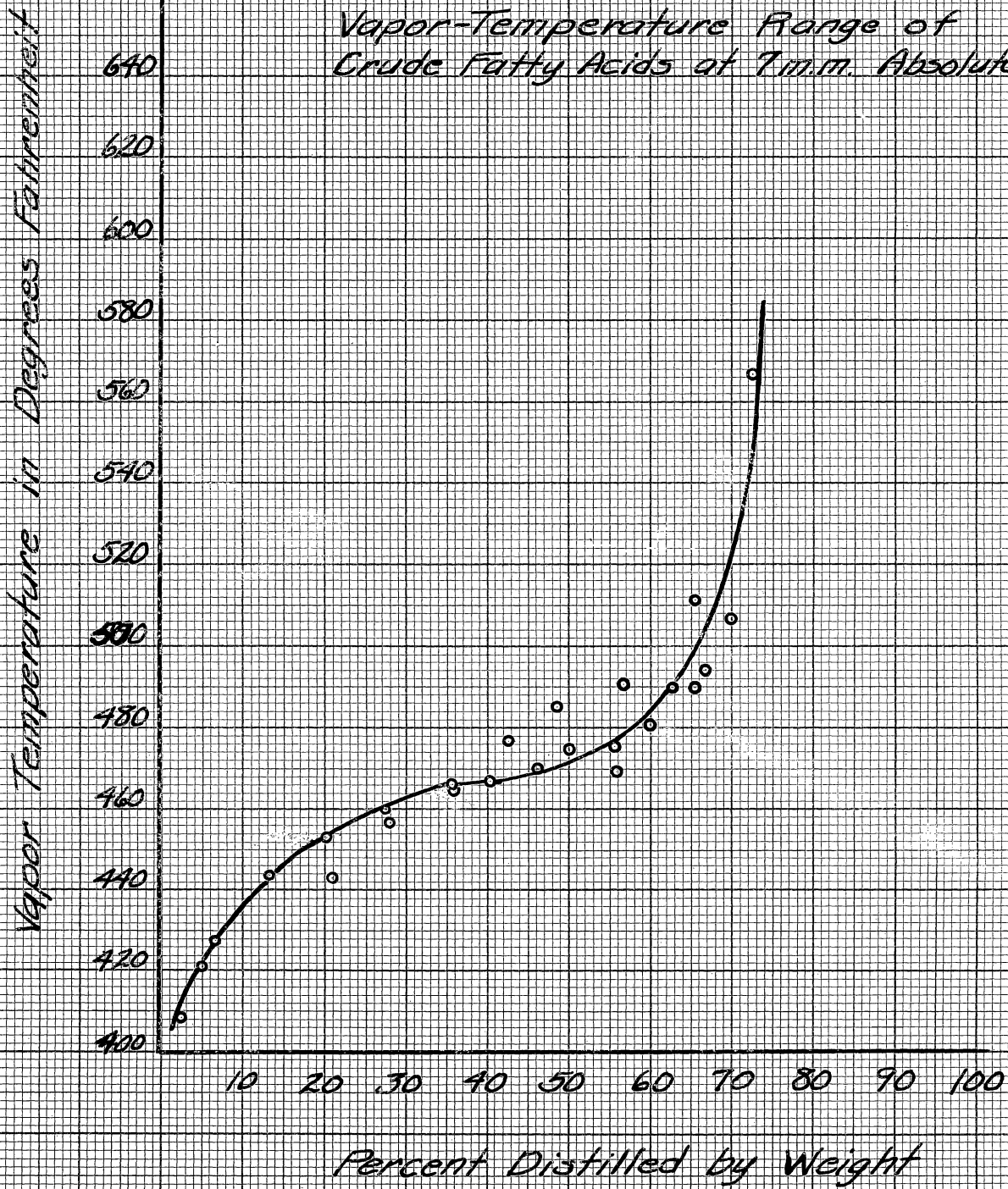
GRAPH VI.

*Percent Fatty Acids in
Distilled Fatty Acid.*

*From Distillations 1, 2, & 3.
at 7 m.m. Absolute Pressure*

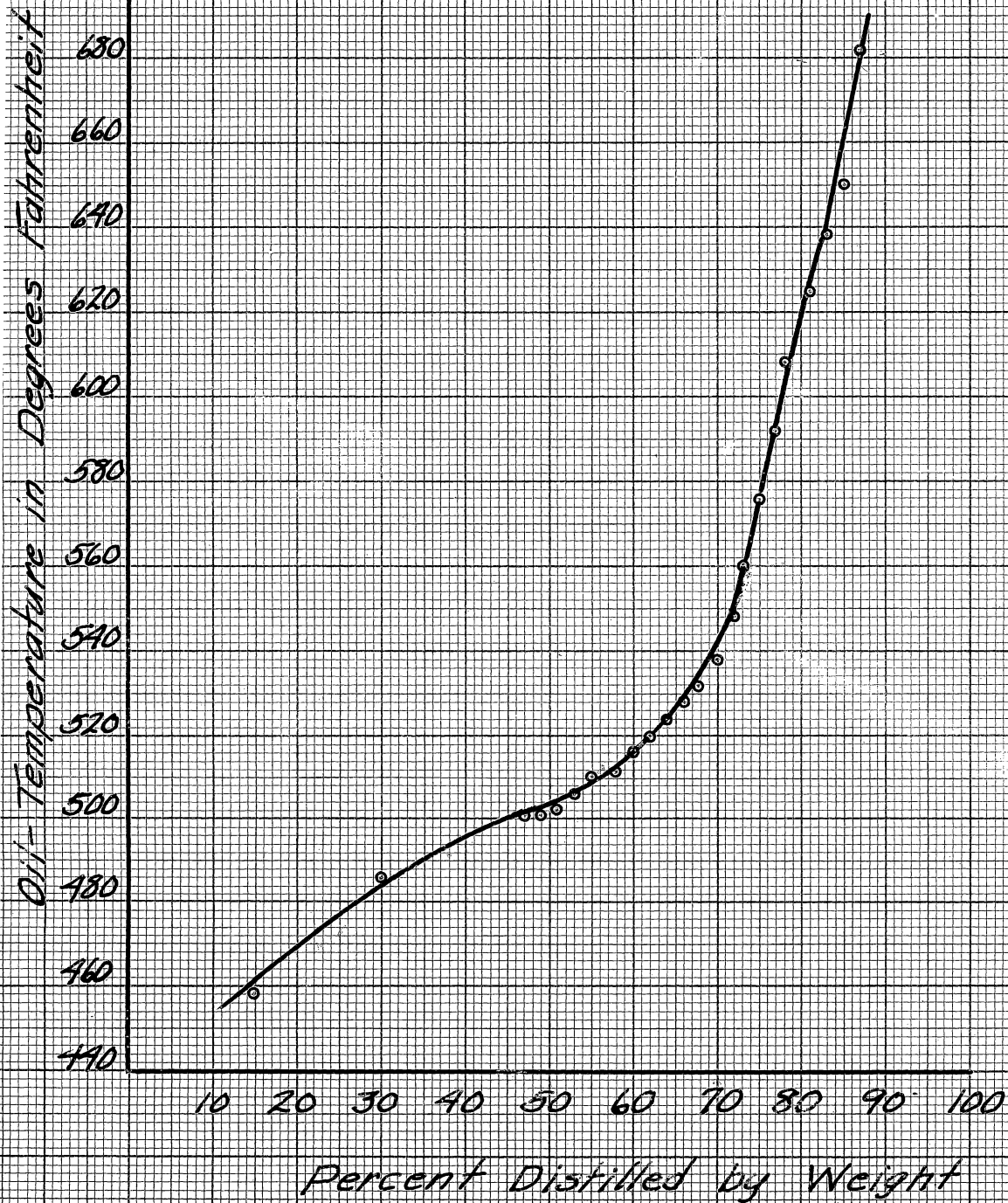
GRAPH VII.

Vapor-Temperature Range of
Crude Fatty Acids at 7mm. Absolute Press.



GRAPH VIII.

Oil - Temperature Range of Crude
Fatty Acids at 7 m.m. Absolute Pressure.



Discussion and Conclusions

The curves illustrating the results of the distillation were plotted on a differential percentage basis in order to more clearly indicate breaks in the curves. The close agreement of the results of the three distillations show that if any errors were present they were relative in their magnitude. Since the results were in such close agreement it was considered permissible to make summation curves for average values.

In distillation No. 1, illustrated by curve I, it is shown that as distillation progresses the rosin content of the distillate rises rapidly from an initial value of 20% when approximately 10% is distilled; while the fatty acid content of the distillate remains fairly constant at a value of 40% for the first 25% of distillate, and then drops off rapidly. The unsaponifiable matter from an initial value of 35% for the first 10% of distillate, drops off rapidly as the distillation progresses. Owing to the freezing of the distillate in the arm of the flask as previously noted, this distillation was not completed. However, it does show that the fatty acids and one part of the unsaponifiable matter constitute the lower boiling constituents, and that the abietic acid is the higher boiling point constituent.

In distillation No. 2 a complete distillation was attained, being stopped only when there was unmistakable evidence that decomposition was taking place. From curve II it is definitely shown that decomposition does take place when approximately 70% is distilled. The trends of the fatty acid content and the unsaponifiable content, as indicated in the first distillation are confirmed. The fatty acid content reaches approximately a constant value of 10% when 50% of the material is distilled. The

unsaponifiable matter, decreasing rapidly at first, reached approximately a constant value of 8% when 53% has been distilled and continued at this value until 70% had been distilled over. At this point the unsaponifiable content began to rise rapidly. The abietic acid content of the distillate rises to a maximum value of 84% when 60% has been distilled over, and at 66% distilled, began to fall rapidly. This decrease in the abietic acid content, coupled with the concurrent rise in the unsaponifiable content, necessitates some explanation. Two interpretations may be placed upon this: first, that the high temperature at this point (540°F_0) caused a decomposition of the abietic acid to form unsaponifiable matter; second, that the unsaponifiable matter originally present is divided into two fractions, one a comparatively low boiling point material and the other a high boiling point material. An examination of the analyses of the original material shows that there was present at the start of the distillation 89 gms. of unsaponifiable matter. When 70% of the crude had been distilled only 12.11 grams of unsaponifiable, out of a total of 89 gms., had been distilled over. From this evidence it is concluded that the second possibility as mentioned above is the correct assumption. A corollary of this is that the pitch or residue consists principally of high-boiling unsaponifiable matter.

In order to more clearly indicate this point, it was decided that in the next distillation approximately half of the material would be distilled off, and then small samples taken over the rest of the distillation. This was done and an inspection of the results clearly shows that there is decomposition taking place.

Both the oil temperature and the vapor temperature curves indicate a break at the point when 70% of the oil is distilled off, shown by a sudden

increase in the rate of temperature rise. This is confirmed by the analyses, which show that when 70% of the oil is distilled, practically all of the available fatty acids and abietic acid have been recovered, and that a continuation of the distillation would only yield an additional amount of the higher boiling unsaponifiable matter, undesirable in any refined oil, and also a darkening of the color of the distillate, which is also highly undesirable.

From the evidence as presented, the following conclusions are drawn:

1. Boiling range of the crude fatty acids, 400°F to 600°F at an absolute pressure of 5-7 mm.
2. It is feasible only to distill 70% of the crude, which will come over at a maximum temperature of 500°F.
3. Approximately 95% of the available fatty acids are distilled over in the first 45% distilled.
4. Approximately 98% of the available fatty acids and 85% of the available abietic acid have been recovered when 70% of the crude is distilled.

PART II

EFFECT OF CHANGE IN ABSOLUTE PRESSURE

EFFECT OF CHANGE IN ABSOLUTE PRESSURE

Introduction

In the previous distillation of crude fatty acids it was noted that there was an apparent decomposition of the abietic acid to form sterols. This division of the research was then undertaken, to determine the minimum absolute pressure at which it is possible to economically distill the material.

The expense of maintaining a high vacuum is well known to the industry, and any increase of the absolute pressure necessary to distill the material would correspondingly decrease the cost of production. The importance of determining this condition, both from a design and a cost of production basis, is indisputable and so their evaluation was attempted.

The raw material selected for this distillation was the crystallized abietic acid. This material was used so that the cracking phenomena could be more clearly distinguished and also, since it is practically pure abietic acid, it was assumed that the crystals would be much more sensitive to changes in absolute pressure than a mixture of materials such as crude fatty acids.

Procedure

Two hundred and fifty pounds of the abietic acid crystals from plant operation were taken as a sample for the following distillations. As near as possible a representative five-pound sample was taken for each distillation, thoroughly mixed and then quartered down to the desired amount, approximately three hundred grams for each distillation.

Four distillations were undertaken in this investigation, one at 5 mm. absolute pressure, one at 25 mm., one at 60 mm., and one at 211 mm. The differences and characteristics of each distillation were noted and analyses run on the distillates.

The sample of abietic acid crystals was weighed into a Claisen flask, stoppered with two rubber stoppers bearing Fahrenheit thermometers, one extending down into the melted crystals and the other located in the vapor outlet of the flask. The temperatures read on these thermometers are designated as the oil temperature ($^{\circ}\text{F}_O$) and the vapor temperature ($^{\circ}\text{F}_V$) respectively. The flask was placed upon an adjustable electric heater of 760 watts capacity. Varying adjustments were needed on the heater as will be explained later. The flask was lagged completely with asbestos rope. The arm of the flask was connected to a Pyrex distilling receiver, containing nine previously weighed tubes. Each of these tubes hold approximately 30 cc. The connection to the vacuum line was made next, and the vacuum turned on at the same time as the heat.

It required about two hours to get the first drop of the distillate over; distillation was complete in another hour. Three temperatures were taken on each tube of distillate caught as near as possible for each 10 cc. distilled.

After the distillation was complete, the heat was turned off and the tubes and flask allowed to cool down, with the vacuum still on. This was done in order to prevent possible oxidation of the material by exposure to the air while hot. The insulation was then removed and the flask and its contents weighed, and the tubes and their contents weighed.

The content of each tube was analyzed after being thoroughly mixed in order to obtain a representative sample. This analysis consisted of a rosin acid number and an acid number, determined as given in the methods of analysis. No analysis was run on the residue in the flask.

From the constants as determined above the content of fatty acids and the abietic acid was determined, and by difference the amount of unsaponifiable matter was determined.

Tables and curves were prepared illustrating the results.

Data and Results

DISTILLATION NO. 4

There was a small amount of gas evolved at the beginning of the distillation. The first drop of distillate came over at 100°F_v . Distillation actually began at 360°F_v , continuing smoothly until a temperature of 493°F_v was reached when gas again became apparent. At a temperature of 593°F_v the gas increased tremendously and then the distillation was stopped. The last portion of the distillate turned a dark brown color as compared to a light straw color for the other samples. The distillate in fractions 1, 2, 3, 4, was liquid, but in all the rest except tube 9 (the last), it solidified after cooling and the tubes had to be broken in order to obtain a sample.

DISTILLATION NO. 4

TABLE IV

Distillation of Abietic Acid Crystals at 5-7 mm. Absolute Pressure

Fraction	Temp. :°F _v	Total :gms.	Acid: :No.	Abietic :Acid :No.	Fatty :Acids :%	Abietic :Acid :%	Sterols :%	Recovery :%
1.	460	31.4	156	115	21.0	62.0	17.0	
2.	468	32.1	178	138	21.0	75.0	4.0	
3.	470	32.8	180	167	6.5	90.0	3.5	
4.	472	26.9	183	176	3.5	95.0	1.5	
5.	473	32.0	183	183	0.0	100.0	0.0	
6.	475	32.0	186	187	0.0	100.0	0.0	
7.	478	30.4	186	184	0.0	100.0	0.0	
8.	482	30.2	184	182	0.0	100.0	0.0	
9.	525	23.3	147	134	7.0	72.0	21.0	
Total Distillate		271.1	--	--	6.6	88.6	4.8	96.1
Residue		5.0						1.8
Loss		6.0						2.1
Abietic Acid Crystals		282	178	161	8.0	87.0	5.0	

DISTILLATION NO. 5

The same procedure was followed in this distillation as in No. 1, except the absolute pressure was raised to 25 mm. The oil temperature at which the distillation began was approximately 60°F higher than in the previous distillation. At the beginning of the distillation approximately one c.c. of a water-like material distilled over into tube 1. The oil began to distill over and formed a layer on top of the supposed water of decomposition. When the tube was nearly full the heat from the oil in the tube apparently caused the water to vaporize and blew the principal portion of the sample out of the tube. No other particular differences were noted.

DISTILLATION NO. 5

TABLE V

Distillation of Abietic Acid Crystals at 25 mm. Absolute Pressure

Fraction	Temp. :°F _v	Total :gms.	Acid :No.	Rosin :Acid :No.	Fatty :Acids :%	Abietic :Acid :%	Sterols :(calc.)	Recovery :%
1.	510	12.3	131	103	15.0	55.0	30.0	
2.	523	23.1	169	137	16.0	74.0	10.0	
3.	524	22.3	174	150	12.0	81.0	7.0	
4.	532	28.3	177	166	5.0	90.0	5.0	
5.	534	28.8	179	171	4.0	92.0	4.0	
6.	536	22.0	176	174	2.0	94.0	4.0	
7.	541	22.4	176	174	2.0	94.0	4.0	
8.	545	24.2	177	162	7.0	87.0	6.0	
9.	550	25.5	164	159	3.0	86.0	11.0	
Total Distillate		208.9	--	--	6.8	85.5	7.7	77.7
Residue		35.0						13.0
Losses		25.1						9.3
Abietic Acid Crystals		269	178	161	8.0	87.0	5.0	

DISTILLATION NO. 6 (60 mm. absolute pressure)

In this distillation the starting oil temperature was approximately 50°F higher than in the previous distillation. Also the same phenomenon of the supposed water of decomposition was observed, and again it vaporized, blowing the contents of the tube out, and the sample was lost.

No other particular differences were noted.

DISTILLATION NO. 6

TABLE VI

Distillation of Abietic Acid Crystals at 60 mm. Absolute Pressure

Fraction	Temp. °F	Total gms.	Acid No.	Rosin Acid No.	Fatty Acids %	Abietic Acid %	Sterols (calc.) %	Recovery %
1.	531	4.1	--	--	--	--	--	
2.	555	32.3	149	106	22.0	57.0	21.0	
3.	562	29.2	168	137	14.0	75.0	11.0	
4.	567	30.2	170	153	9.0	82.0	9.0	
5.	570	24.2	172	158	7.0	85.0	8.0	
6.	572	25.6	176	162	7.0	87.0	6.0	
7.	573	24.0	173	161	6.0	87.0	7.0	
8.	573	24.4	169	159	5.0	86.0	9.0	
9.	575	25.2	161	156	3.0	84.0	13.0	
Total Distillate		219.2	--	--	9.8	79.5	10.7	73.0
Residue		41.0						13.7
Loss		39.8						13.3
Abietic Acid Crystals		300	178	161	8.0	87.0	5.0	

DISTILLATION NO. 7 (211 mm. absolute pressure)

A rise of 60°F in the starting temperature of the oil was noted in this distillation. The water decomposition came over this time also but did not vaporize, and so the first sample was obtained.

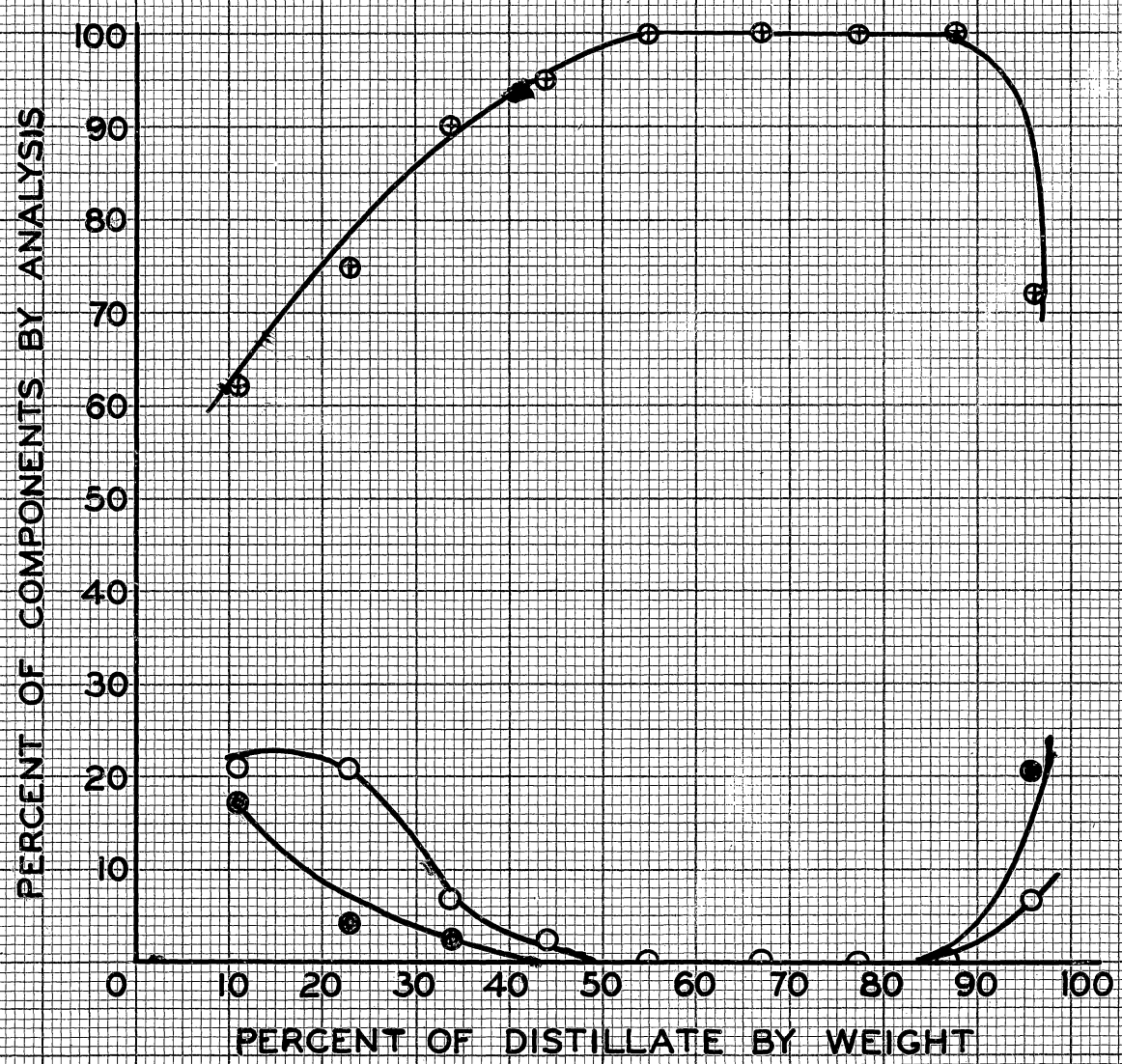
Temperatures became too high to complete the distillation before all of the tubes were full.

DISTILLATION NO. 7

TABLE VII

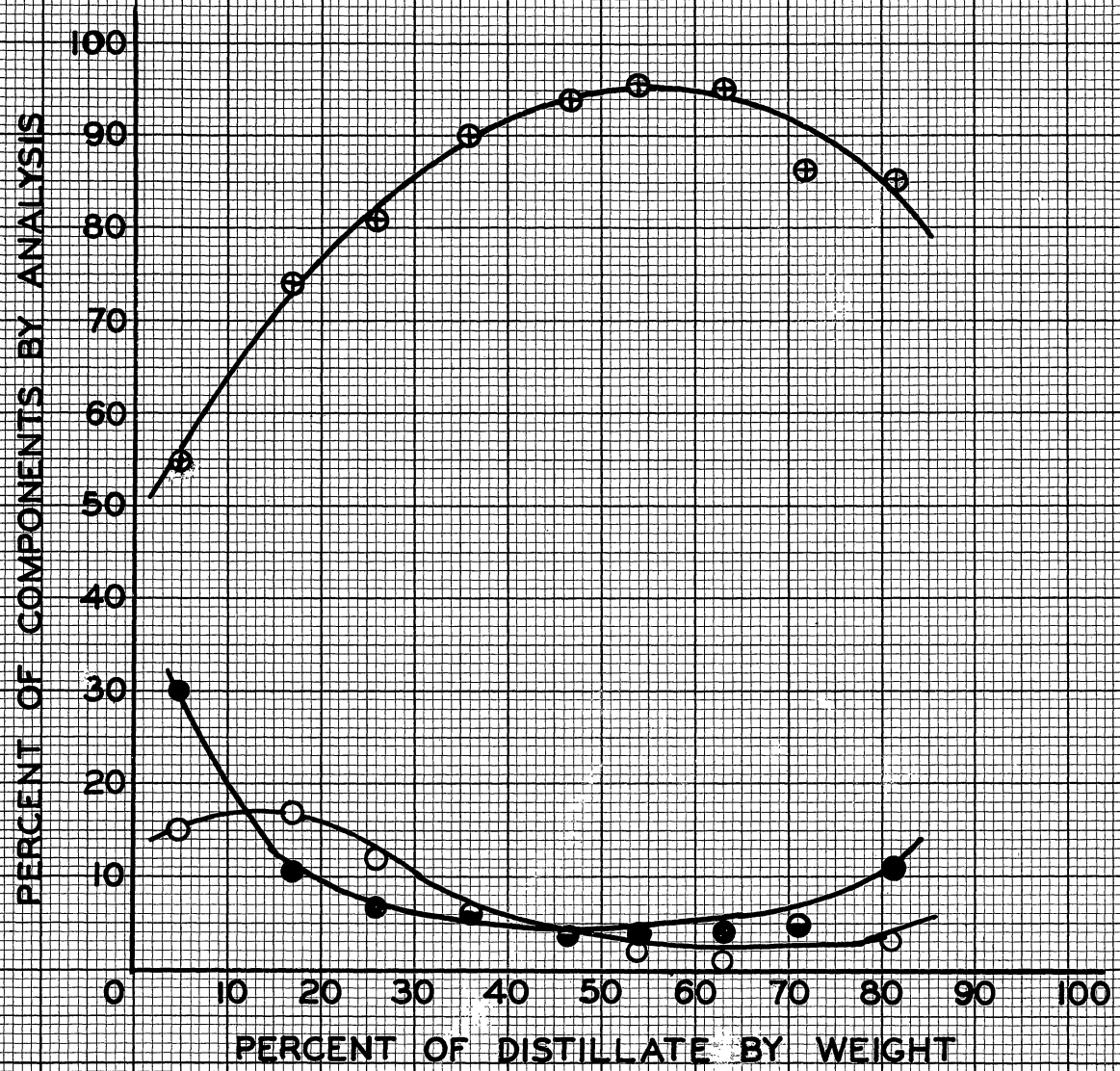
Distillation of Abietic Acid Crystals at 211 mm. Absolute Pressure

Fraction	Temp. °F _v	Total gms.	Acid No.	Resin Acid No.	Fatty Acids %	Abietic Acid %	Sterols (calc) %	Recovery %
1.		29.4	127	76	27.0	41.0	32.0	
2.		32.8	98	83	7.0	45.0	48.0	
3.		30.8	92	68	12.0	37.0	51.0	
4.		25.7	113	100	6.0	54.0	40.0	
5.		24.6	128	117	6.0	63.0	31.0	
6.		24.9	131	123	4.0	66.0	30.0	
7.		24.2	130	127	2.0	68.0	30.0	
8.		23.6	126	125	0.0	68.0	32.0	
9.		24.6	110	110	0.0	60.0	40.0	
Total Distillate		238.6	--	--	7.6	54.4	38.0	79.3
Residue		31.0						10.3
Loss		31.0						
Abietic Acid Crystals		300.6	178	161	8.0	87.0	5.0	



DISTILLATION OF
 ABIETIC ACID CRYSTALS
 GRAPH NO IX
Absolute Pressure 7 mm.

- FATTY ACID
- ⊗ ABIETIC ACID
- STEROLS (CALC.)

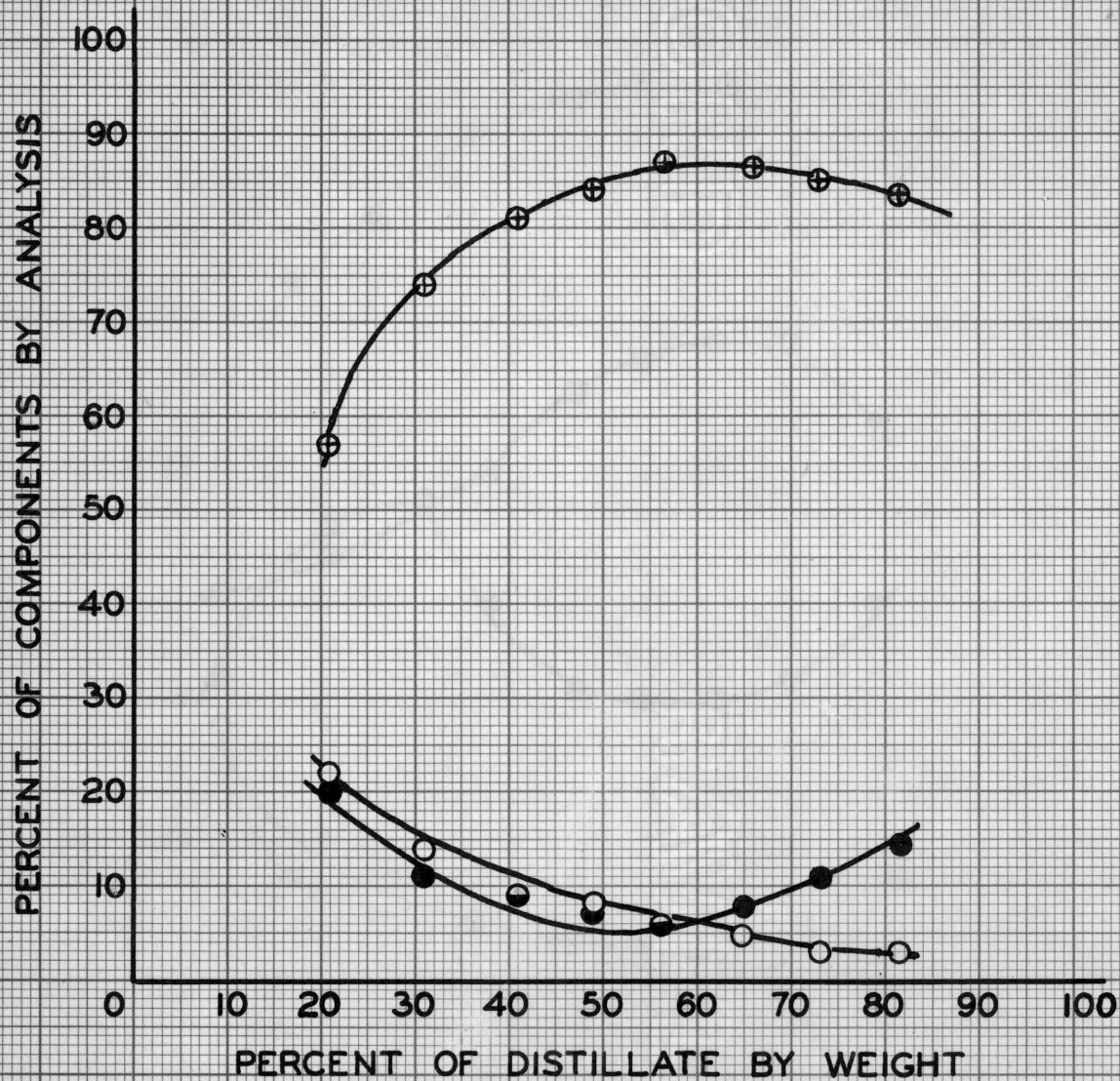


DISTILLATION OF ABIETIC ACID CRYSTALS

GRAPH NO. X

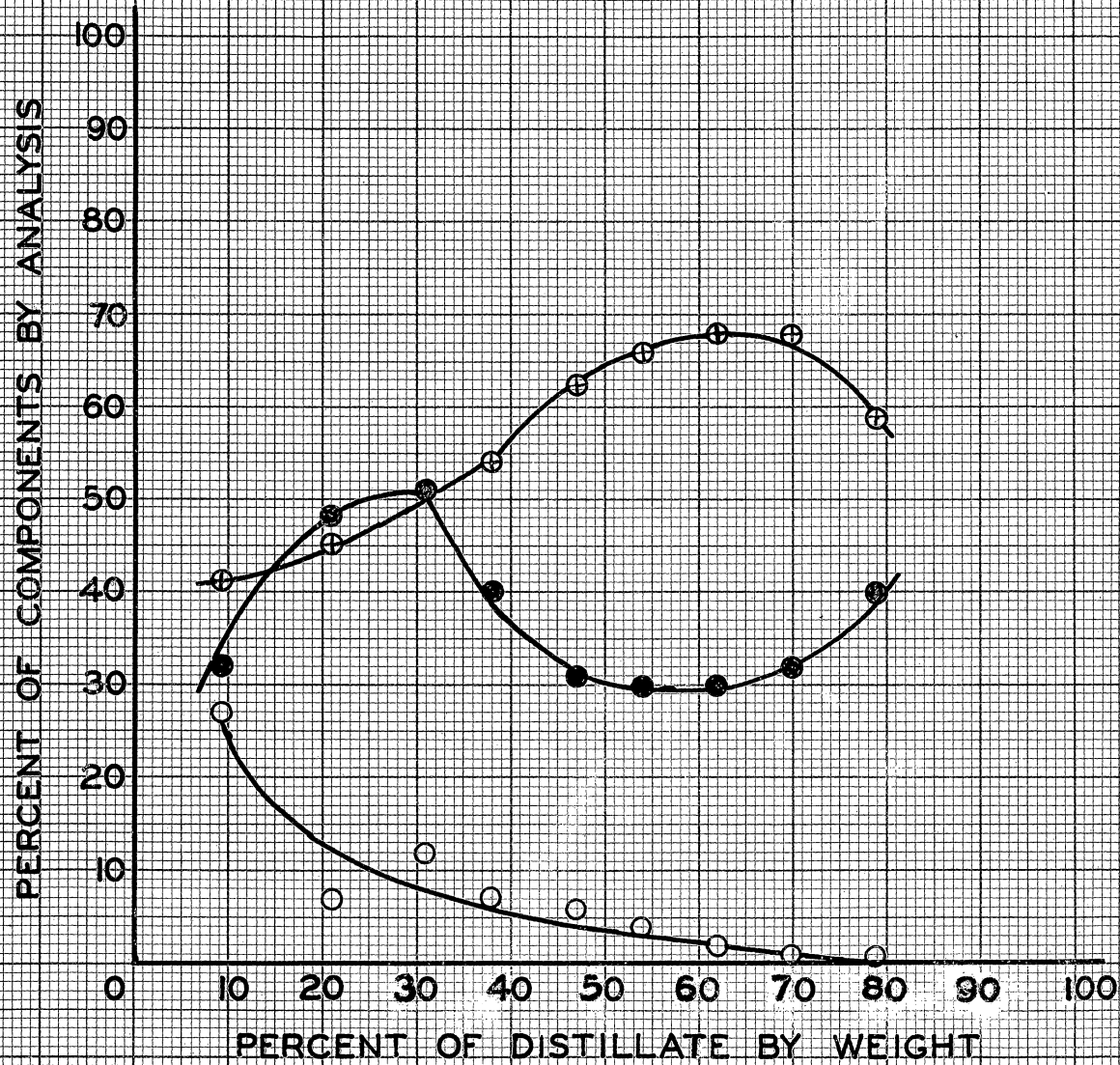
Absolute Pressure 25 mm.

- FATTY ACID
- ⊕ ABIETIC ACID
- STEROLS (CALC.)



DISTILLATION OF
ABIETIC ACID CRYSTALS
GRAPH NO **XI**
Absolute Pressure 60 m.m.

- FATTY ACID
- ⊕ ABIETIC ACID
- STEROLS (CALC.)



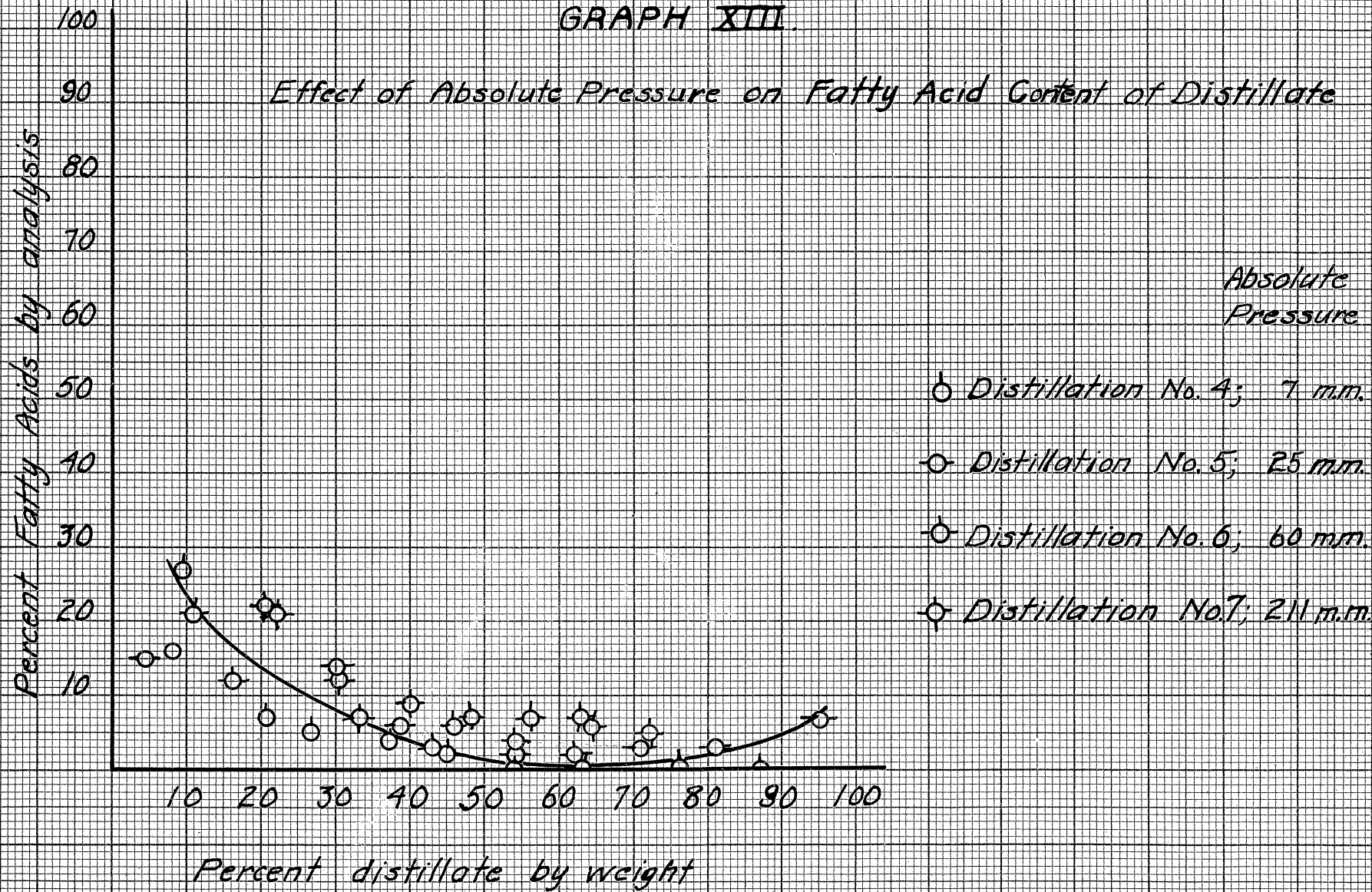
DISTILLATION OF
 ABIETIC ACID CRYSTALS
 GRAPH NO **XI**
Absolute Pressure 211 mm.

- FATTY ACID
- ⊕ ABIETIC ACID
- STEROLS (CALC.)

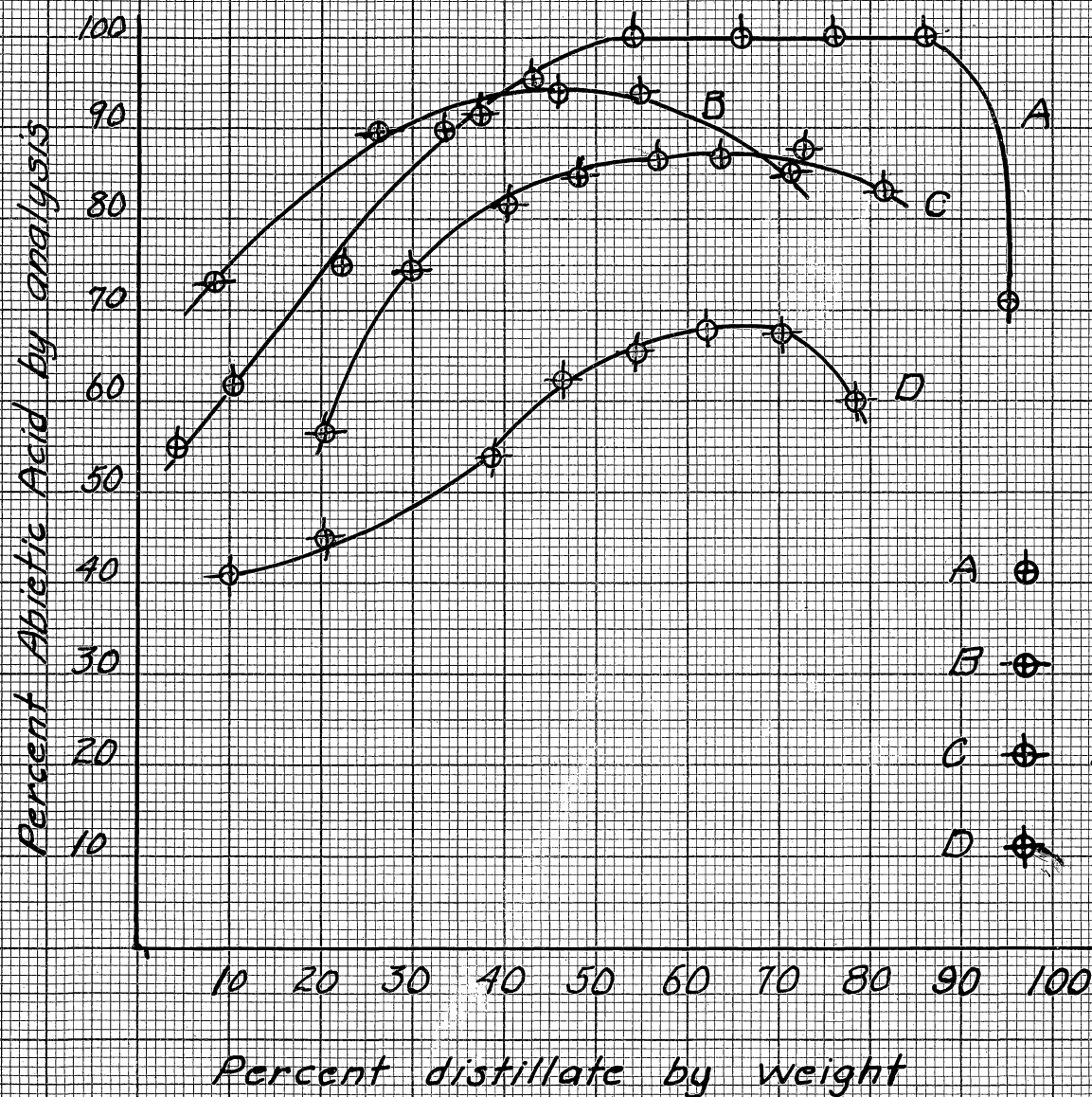
VA. (108) 12111-100, JUNIOR, LITHO

GRAPH XIII.

Effect of Absolute Pressure on Fatty Acid Content of Distillate



Effect of Absolute Pressure on Abietic Acid Content of Distillate



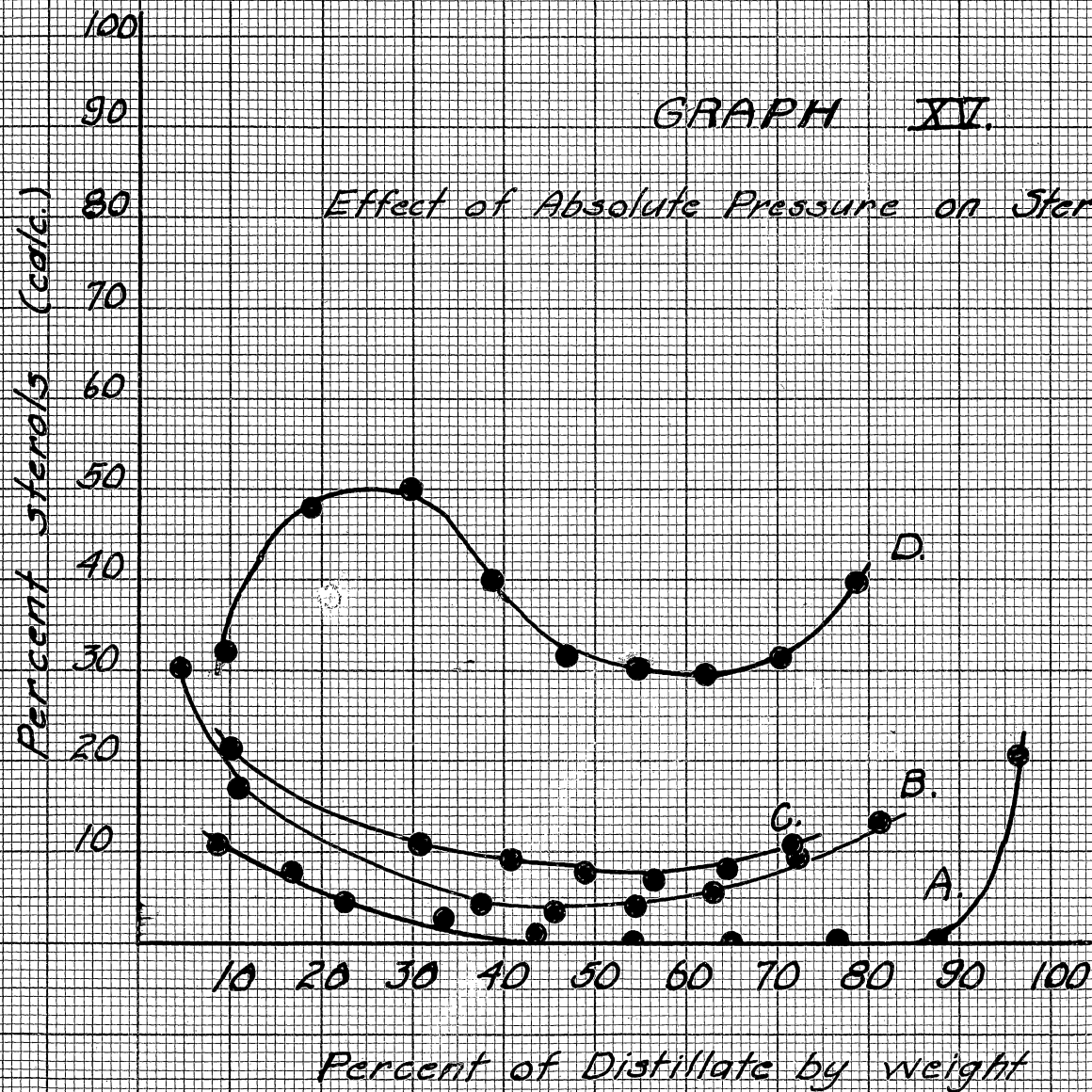
Absolute Pressure

A ⊕ Distillation No. 4; 7 m.m.

B ⊕ Distillation No. 5; 25 m.m.

C ⊕ Distillation No. 6; 60 m.m.

D ⊕ Distillation No. 7; 211 m.m.



*Absolute
Pressure*

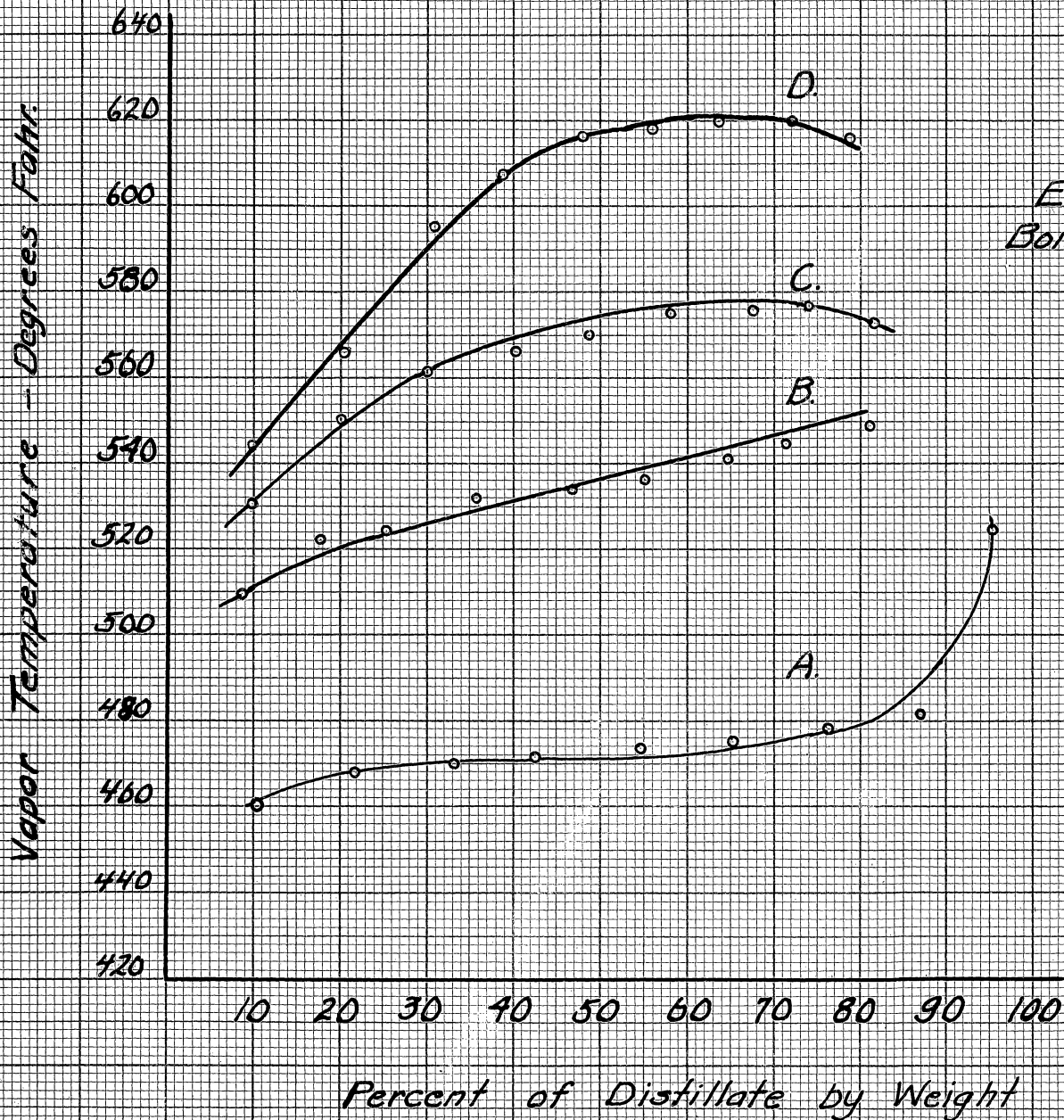
A. Distillation No. 4; 7 m.m.

B. Distillation No. 5; 25 m.m.

C. Distillation No. 6; 60 m.m.

D. Distillation No. 7; 211 m.m.

NO. 1000000000 TO 10000000000



GRAPH XVI.

Effect of Absolute Pressure on Boiling Range of Crude Fatty Acid

Absolute Pressure

A. Distillation No. 4; 7 m.m.

B. Distillation No. 5; 25 m.m.

C. Distillation No. 6; 60 m.m.

D. Distillation No. 7; 211 m.m.

Discussion

In distillation No. 4 everything ran as expected with no differences from the original crude fatty acid distillation in so far as the actual physical characteristics of the distillation were concerned. However, when an examination of the tubes of distillate (after cooling) was made it was noted that the contents of the first four tubes was liquid, the contents of the next four had solidified, and the last tube was liquid. No crystallization was noted in any of the tubes. This may be explained by the fact that the second four tubes contained pure abietic acid which solidified upon cooling. The contents of the first four tubes were diluted by a certain amount of fatty acids and unsaponifiable matter and thus the melting point was lowered below that of room temperature. In the case of the last tube it probably contained sufficient decomposition products to accomplish the same result.

These assumptions are borne out by the analysis (Table III) which shows that up to the fourth tube fatty acids and unsaponifiable matter were present, that the second four tubes contained pure abietic acid, and fatty acids and unsaponifiable matter were present in the last tube.

Distillation No. 5 was conducted in exactly the same manner as No. 4, with the exception of the absolute pressure which was raised to 25 mm.

At the start of this distillation it was noted that approximately one cc. of a material resembling water distilled over later vaporizing suddenly and blowing most of the contents of the first tube out, causing considerable loss on that sample. This material must have been water of decomposition, for no other substance would have had sufficient vapor pressure to cause such sudden and complete vaporization. The crystals themselves contained no water of crystallization or any moisture. In addition, no similar phenomenon was observed in the first distillation.

Other differences noted in this distillation were a 50°F rise in the initial boiling point (Curve VIII); the abietic acid content of the sampling tubes at a maximum of 94% as compared to 100% in the first distillation; a 76.7% abietic acid total recovery as compared to 97.8% in No. 1.

It should be pointed out that due to the fact that approximately one half of the first sample was lost the above figure for the recovery of abietic acid is low. However, allowing for the maximum recovery possible the figure would not exceed 80.7%.

In addition, it is noted that only 66.5% of the fatty acids originally present were recovered (Table IV). This figure is in error, and estimating the amount lost we conclude that the actual recovery is probably in the neighborhood of 90%. In the case of the unsaponifiable matter it is noted that the recovery is 122%. This is also low, and the estimated recovery is 130%. This evidence points unmistakably to the fact that the abietic acid is decomposing to form unsaponifiable matter.

Distillation No. 6 was conducted in the same manner with the absolute pressure raised to 60 mm. Examining the results of this distillation as was done with No. 2, we find that the per cent of abietic acid recovered drops to 65.5%, estimated at 70%. The per cent unsaponifiable rises to 153%, estimated to be 160%. The fatty acid recovery is approximately the same as in the previous distillation, at 87% and estimated to be 95%. The small quantities involved in the fatty acid content cause a reduction in the precision of the results, which on a percentage basis becomes greatly magnified. It is then permissible to assume that the fatty acid recovery for No. 2 and No. 3 are the same.

Following the same method of interpretation for distillation No. 7

which was carried out at an absolute pressure of 211 mm., it was found that the abietic acid recovery drops to 49.6%; the unsaponifiable rises to 600%; the fatty acid drops to 75%. In this case the first sample was not lost and so the percentages are correct as stated.

Conclusions

From the evidence as presented it is concluded that the abietic acid decomposes, when the absolute pressure is increased, to form unsaponifiable matter. It also proves that the distillation of this and related material such as crude fatty acids should be carried out at absolute pressures not greater than 7 mm.

It is also evident that it is not possible to produce fatty acid by cracking of abietic acid by means of absolute pressure variations.

PART III

CORROSION CHARACTERISTICS

Introduction

In plant practice it had been found that stills constructed of 18-8 stainless steel corroded very rapidly, and that copper was fairly resistant to the corrosive action of the crude fatty acids. Therefore, copper was used for the construction of the additional stills. However, copper did not prove at all satisfactory as a material of construction because of scaling and pitting. Scale formation constituted a tremendous handicap in the operation of the still, cutting the rate of heat transfer to such an extent that it was necessary to clean the stills at least once a week in order to secure average results from the distillation. This scale removal also increased the rate of corrosion because fresh surface was exposed to corrosive attack. In addition to this undesirable situation, pitting of the copper occurred to such an extent that 1/4" thick tubes had an effective life of only three months. This fact entailed a tremendous replacement charge on the still; coupled with the cost of replacement of insulation on the stills after cleanout periods, the net result was to double the cost of refining the crude fatty acids.

This research was undertaken in order to discover, if possible, some metal or alloy of construction that would be resistant to the corrosive action of the crude fatty acids, or that would not be subject to scaling and pitting. Such a result, if obtained, would mean not only that the cost of refining the crude fatty acids could be reduced to half its former value but also that the capacity of the stills would be doubled with no increase in size.

The only reference in the literature was by de Keghel (68) who, in 1927, reported that tallol on boiling six hours appreciably attacked wrought iron, cast iron, copper, zinc, tin, nickel, and aluminum slightly.

Therefore, for the purpose of this investigation a series of twenty-four metals and alloys of construction were selected, embracing almost every general type of metals and alloys available for commercial use in still construction.

Procedure

The test used for determination of the corrosion resistance of the test specimens was an adaptation of the standard static corrosion test as outlined in Perry, "Chemical Engineers' Handbook" (69). ✓

Equipment

A solid nickel kettle, 9.5" in diameter and 10" depth was placed on an electric hot plate and approximately two gallons of crude fatty acids poured in and brought to temperature. The samples, after careful weighing and calipering, were suspended from the cover of the kettle by means of glass rods arranged so that the samples were not in contact with each other or with the container. Next the glass stirrer shaft was connected to the motor and the speed adjusted by means of a rheostat to 300 r. p. m. Then a thermostat bulb was placed in a thermometer well on the cover and adjusted to maintain the temperature as near as possible to 580° F. Actually the temperature varied from 560-590°^F which was as close control as was possible with the equipment available.

Corrosion Treatment

A sample of the crude fatty acid was taken at the beginning and end of each run and an acid number run on it in order to determine the extent to which decomposition was taking place during the course of the run.

At the end of 24 hours the samples were removed and weighed and then returned to the bath for an additional 48 hours at which time they were again removed and weighed. Temperatures were read continuously during each run at each hour with a few exceptions.

Specimen

No special treatment of the test specimens was resorted to in any case,

since it was desired to approximate as near as possible conditions as they would actually be encountered in the plant. The samples were first sheared to approximate size of one inch by two inches, then drilled for the glass suspension rod and the rough edges smoothed out with a file. This was not followed by annealing.

Final Treatment of Specimen

At the end of the test period the samples were removed from the bath, washed twice in kerosene and wiped clean and dry with clean bleached sheeting, and then washed again in carbon tetrachloride. After weighing the samples were compared with the original samples by microscopic examination. No grinding to remove pits was resorted to, nor was any attempt made to evaluate the depth of pitting.

Corrosion Rate Formula

In all cases the corrosion rate was expressed as inches penetrated per year, calculated according to the formula as given in Perry, (69) p. 1725, as follows:

$$C = \frac{24 \times 360 \times W}{(2.54)^3 \times A \times S \times T}$$

Where

C = inches penetrated per year

W = loss in weight in grams

S = specific gravity in grams/cubic centimeter

T = time of exposure in hours.

A = area of test specimen

TABLE I

Twenty-four Hour Low Temperature Corrosion Test

Sample	Material	Area Sq. In.	Wt. Loss Gms.	Inch Penetration Per Year $\times 10^{-3}$
I-#1	99.4% Al	4.30	0.0023	2.16 $\times 10^{-3}$
I-#2	99.4% Al	4.32	0.0028	2.63
I-#3	99.4% Al	4.85	0.0025	2.09

Time - 24 hours

Temperature - 395° - 410° F.

Corroding Agent - Crude fatty acids

Acid Value - Start 142; finish 79

In this test the samples were suspended from a wooden stirrer shaft, which was then rotated.

TABLE II

Twenty-four Hour High-Temperature Corrosion Test

Sample	Composition						Area	Wt. Loss	Inch Penetration
Number	Cr	Ni	Fe	Cu	Mn	Al	Sq. In.	Gms.	Per Year $\times 10^{-3}$
II-1	:	:	:	:	:	:99.4	4.30	0.0014	2.64 $\times 10^{-3}$
II-2	:	:	:	:	:	:99.4	4.32	0.0030	5.65 "
3	:	:	:	:	:	:99.4	4.68	0.0022	3.80 "
4	29	9	Bal.	:	:	Bal.	6.23	0.0017	0.76 "
5	18	22	Bal.	:	:	Bal.	5.62	0.0060	3.00 "
6	:	68	:	29	:	:	8.00	0.0429	13.4 "
7	:	68	:	29	:	:	8.00	0.0370	11.6 "
8	:	:	Bal.	:	1.25	Bal.	4.80	0.0027	4.56 "
9	:	:	Bal.	:	1.25	Bal.	4.66	0.0035	6.09 "

Time: 24 hours

Temperature Range: 570° - 590° F.

Corroding Agent: Crude fatty acids

Acid Value: Start, 139; finish, 75

TABLE III

Seventy-two Hour High-Temperature Corrosion Test

Sample Number	Composition					Area Sq. In.	Wt. Loss Gms.	Inch Penetration Per Year x 10 ⁻³
	Cr	Ni	Fe	Mg	Al			
III-1	:	:	:	:	:99.4	4.30	0.0456	28.0
2	:Yes	:	:	:Yes	:98	4.64	0.0472	27.4
3	:Yes	:	:	:Yes	:98	4.44	0.0430	26.3
4	:12	:80	:8	:	:	8.00	0.0014	0.15
5	:12	:80	:8	:	:	8.00	0.0009	0.10

Time: 72 hours
 Temperature Range: 570° - 595° F.
 Corroding Agent: Crude fatty acids
 Acid Value: Start, 115; finish, 64

TABLE IV-A

Twenty-four Hour High-Temperature Corrosion Test

Sample	Composition					Area	Wt. Loss	Inch Penetration
Number	Cr	Ni	Fe	Mo	Mn	Sq. In.	Gms.	Per Year x 10 ⁻³
IV-1	12.7	0.3	Bal.			5.24	2.8830	1550.0
IV-2	17.7	10.8	Bal.	2.3		5.25	0.0033	1.77
3	17.8	8.8	Bal.			4.70	0.0500	29.9
4	17.7	0.2	Bal.			4.99	2.1770	1230.0
5	16.7	8.3	Bal.			4.98	0.0380	21.4
6	17.8	12.7	Bal.	2.9		4.00	0.0048	3.38
7	25.2	19.9	Bal.			4.93	0.0048	2.74
8	22.2	10.4	Bal.			4.78	0.0110	6.49
9		58.0	20.0	20.0	2.0	4.25	0.0224	14.90
10	25.	20	Bal.			4.70	0.0081	4.80
11	29	9	Bal.			6.23	0.0025	1.12

Time: 24 hours

Temperature Range: 520° - 560° F.

Corroding Agent: Crude fatty acids

Acid Value: Start, 146; finish, 95

TABLE IV-B

Seventy-two Hour High-Temperature Corrosion Test

Sample Number	Composition					Area	Wt. Loss	Inch Penetration
	Cr	Ni	Fe	Mo	Mn	Sq. In.	Gms.	Per Year x 10 ⁻³
IV-1	12.7	0.3	Bal.			5.24	7.8280	1400.0
IV-2	17.7	10.8	Bal.			5.25	0.0058	1.04
3	17.8	8.8	Bal.			4.70	0.1760	35.10
4	17.7	0.2	Bal.			4.99	6.5562	1235.0
5	16.7	8.3	Bal.			4.98	0.1432	27.0 Y
6	17.8	12.7	Bal.	2.9		4.00	0.0072	1.69
7	25.2	19.9	Bal.			4.93	0.0058	1.11
8	22.2	10.4	Bal.			4.78	0.0292	5.73
9		58	20	20	2	4.25	0.0344	7.60
10	25	20	Bal.			4.70	0.0266	5.25
11	29	9	Bal.			6.23	0.0025	0.374

Time: 72 hours
 Temperature Range: 560° - 590° F.
 Corroding Agent: Crude fatty acids
 Acid Value: Start, 146; finish, 62

TABLE V-A

Twenty-four Hour High-Temperature Corrosion Test

Sample Number	Composition					Area	Wt. Loss	Inch Penetration
	Cr	Ni	Fe	Mo	Mn	Sq. In.	Gms.	Per Year x 10 ⁻⁵
V-1	12.7	0.3	Bal.			5.09	4.1560	2300.0
V-2	17.7	10.8	Bal.	2.3		5.49	0.0004	0.206
3	17.8	8.8	Bal.			4.93	0.1972	113.0
4	17.7	0.2	Bal.			5.06	4.1874	2335.0
5	16.7	8.3	Bal.			5.20	0.1435	77.7
6	22.2	10.4	Bal.			4.52	0.0035	2.18
7	25.2	19.9	Bal.			4.10	0.0070	4.83
8	17.8	12.7	Bal.	2.9		4.28	0.0024	1.58
9		58.		20	2	4.21	0.0236	15.8
10	25	20	Bal.			4.60	0.0118	7.25
11	29	9	Bal.			6.43	0.0010	0.434

Time: 24 hours

Temperature Range: 575° - 590° F.

Corroding Agent: Crude fatty acids

Acid Value: Start, 146; finish 90

TABLE V-B

Seventy-two Hour High-Temperature Corrosion Test

Sample Number	Composition						Area	Wt. Loss	Inch Penetration
	Cr	Ni	Fe	Mo	Mn	Si	Sq. In.	Gms.	Per Year x 10 ⁻³
V-1	12.7	0.3	Bal.				5.09	7.6670	1410.0
V-2	17.8	10.8	Bal.	2.3			5.49	0.0004	0.0685
3	17.8	8.8	Bal.				4.93	0.3225	61.4
4	17.7	0.2	Bal.				5.06	7.4349	1375.0
5	16.7	8.3	Bal.				5.20	0.2240	4076 35.0
6	22.2	10.4	Bal.				4.52	0.0050	1.00
7	25.2	19.9	Bal.				4.10	0.0090	2.06
8	17.8	12.7	Bal.	2.9			4.28	0.0030	0.657
9		58		20	2		4.21	0.0311	6.92
10	25	20	Bal.			2	4.60	0.0305	6.22
11	29	9	Bal.				6.43	0.0010	0.145

Time: 72 hours

Temperature Range: 575° - 590° F.

Corroding Agent: Crude fatty acids

Acid Value: Start, 146; finish 55

TABLE VI-A

Twenty-four Hour High-Temperature Corrosion Test

Sample	Composition									Area	Wt. Loss	Inch Penetration
Number	Cr	Ni	Fe	Mo	Mn	Si	Cu	Ta	Sq. In.	Gms.	Per Year $\times 10^{-3}$	
VI-1	18	22	Bal.	1		3			5.44	0.0039	2.01 $\times 10^{-3}$	
VI-2	20	25	Bal.			1			4.59	0.0255	15.7	
3	14	58	6	17					5.11	0.0032	1.76	
4			Bal.			14.5			7.93	0.0025	0.886	
5	0.35		Bal.				0.35		5.66	1.5355	764.0	
6	0.35		Bal.				0.35		4.86	1.3164	764.0	
7	12	80	8						8.00	0.0179	5.76	
8		68					29		8.00	0.0430	13.30	
9		99							8.00	0.0400	12.80	
10								99	1.96	0.0010	0.25	
11								99	1.96	0.0005	0.113	
12							99		7.86	0.0040	1.26	
13							99		7.31	0.0715	24.3	

Time: 24 hours

Temperature Range: 550° - 570° F.

Corroding Agent: Crude fatty acids

Acid Value: Start, 142; finish 102

TABLE VI-B

Seventy-two Hour High-Temperature Corrosion Test

Sample	Composition								Area	Wt. Loss	Inch Penetration
Number	Cr	Ni	Fe	Mo	Mn	Si	Cu	Ta	Sq. In.	Gms.	Per Year x 10 ⁻³
VI-1	18	22	Bal.	1		3			5.44	0.0060	1.04
VI-2	20	25	Bal.			1			4.59	0.0275	5.62
3	14	58	6	17					5.11	0.0052	0.955
4			Bal.			14.5			7.93	0.0041	0.485
5	0.35		Bal.				0.35		5.66	2.6230	434.0
6	0.35		Bal.				0.35		4.86	2.2345	434.0
7	12	80	8						8.00	0.0201	2.15
8		68					29		8.00	0.0790	8.23
9		99							8.00	0.0445	4.74
10								99	1.96	0.0010	0.225
11								99	1.96	0.0005	0.113
12								99	7.86	0.0115	1.21
13								99	7.31	0.0905	10.20

Time: 72 hours

Temperature Range: 560° - 590° F.

Corroding Agent: Crude fatty acids

Acid Value: Start, 142; finish, 61

TABLE VII

Maximum Corrosion Rate of All Test Metals

Sample Number	Composition										Inches Penetration	Scaling	Pitting
	Cr	Ni	Fe	Mo	Mn	Si	Cu	Ta	Al	Mg	Per Year x 10 ⁻⁵ (Max)		
VII-1	:17.7:	0.2:	Bal.:	:	:	:	:	:	:	:	2340.0 x 10 ⁻⁵	: Yes	: Marked
VII-2	:12.7:	0.3:	Bal.:	:	:	:	:	:	:	:	2300.0	: "	: "
3*	:0.35:	:	Bal.:	:	:	:	0.35:	:	:	:	764.0	: "	: "
4	:17.8:	8.8:	:	:	:	:	:	:	:	:	113.0	: "	: "
5	:16.7:	8.3:	Bal.:	:	:	:	:	:	:	:	77.7	: "	: "
6	:	:	:	:	1.25:	:	:	:	Bal.:	:	52.2	: "	: Yes
7	:	:	:	:	:	:	:	:	99:	:	28.0	: "	: "
8	: Yes:	:	:	:	:	:	:	:	98:	Yes:	27.4	: "	: "
9	:	:	:	:	:	:	99:	:	:	:	24.3	: "	: "
10	:	58:	20:	20:	2:	:	:	:	:	:	15.8	: "	: "
11	: 20:	25:	Bal.:	:	:	1:	:	:	:	:	15.7	: Slight	: Slight
12	:	68:	:	:	:	:	29:	:	:	:	13.3	: Yes	: Yes
13	:	99:	:	:	:	:	:	:	:	:	12.8	: "	: Slight
14	: 25:	20:	Bal.:	:	:	2:	:	:	:	:	7.25	: No	: No
15	:22.2:	10.4:	Bal.:	:	:	:	:	:	:	:	6.49	: "	: "
16	: 12:	80:	8:	:	:	:	:	:	:	:	5.76	: "	: "
17	:17.8:	12.7:	Bal.:	2.9:	:	:	:	:	:	:	3.38	: "	: "
18	:25.2:	19.9:	Bal.:	:	:	:	:	:	:	:	2.74	: "	: "
19 ^o	: 18:	22:	Bal.:	:	:	:	:	:	:	:	2.01	: Slight	:
20	:17.7:	10.8:	Bal.:	2.3:	:	:	:	:	:	:	1.77	: No	: No
21 ^o	: 14:	58:	6:	17:	:	:	:	:	:	:	1.76	: No	: No
22	: 29:	9:	Bal.:	:	:	:	:	:	:	:	1.12	: No	: No
23 ^o	:	:	Bal.:	:	:	14.5:	:	:	:	:	0.886	: Slight	:
24	:	:	:	:	:	:	99:	99:	:	:	0.250	: No	: No

Corroding Agent: Crude fatty acids

* Cast iron

^o Rough surface before test

TABLE VIII

Maximum Corrosion Rate of Chromium-Nickel-Molybdenum-Iron Alloy Steels

Sample	Composition				Inches Penetration	Scaling	Pitting
Number	Cr	Ni	Mo	Fe	Per Year x 10 ⁻³ (Max)		
VIII-1	17.7	0.2		Bal.	2340.0	Marked	Marked
VIII-2	12.7	0.3		Bal.	2300.0	Marked	Marked
3	17.8	8.8		Bal.	113.0	Yes	Yes
4	16.7	8.3		Bal.	77.7	Yes	Yes
5	20.0	25		Bal.	15.7	Slight	Slight
6	22.2	10.4		Bal.	6.49	No	No
7	17.8	12.7	2.9	Bal.	3.38	No	No
8	25.2	19.9		Bal.	2.74	No	No
9	17.7	10.8	2.3	Bal.	1.77	No	No
10	29	9		Bal.	1.12	No	No

Corroding Agent: Crude fatty acids

Temperature: 560 - 595°F

Temperature: 560 - 595°F

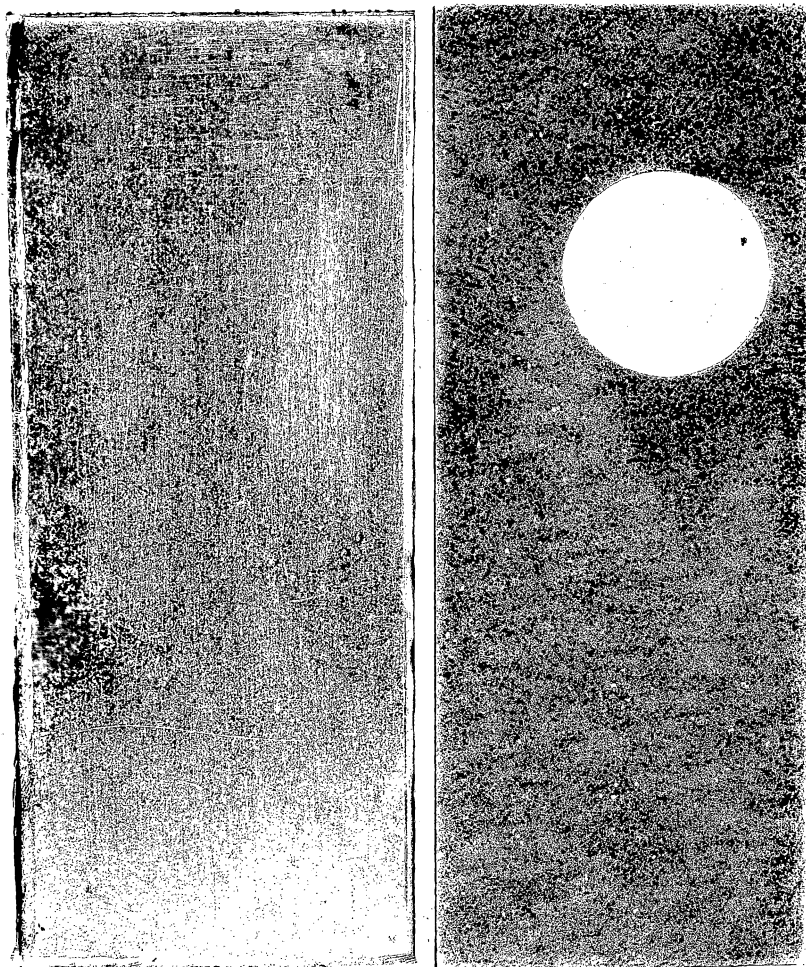


PLATE I
Corrosion Test Specimen

Left hand: Before exposure
Right hand: After exposure
Corroding agent: Crude fatty acids
Temperature: 570°-595° F
Time of exposure: 72 hours
Photograph: Two diameters
Composition of specimen: Cr: 12.66
Ni: 0.32
Fe: Balance

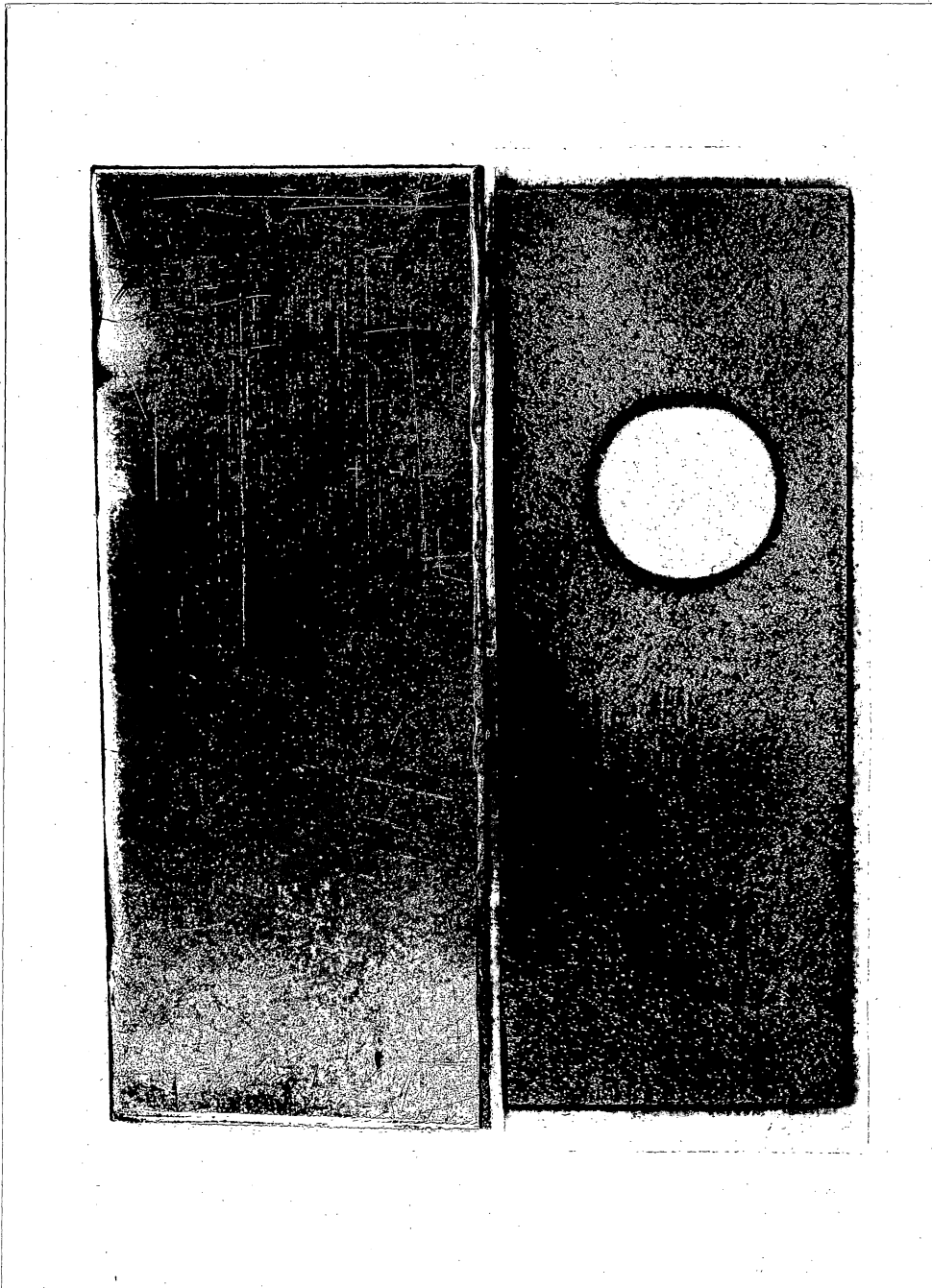


PLATE II
Corrosion Test Specimen

Left hand: Before exposure
Right hand: After exposure
Corroding agent: Crude fatty acids
Temperature: 570°-590° F
Photograph: Two diameters
Time of exposure: 72 hours
Composition of specimen: Cr: 17.66
Ni: 0.24
Fe: Balance

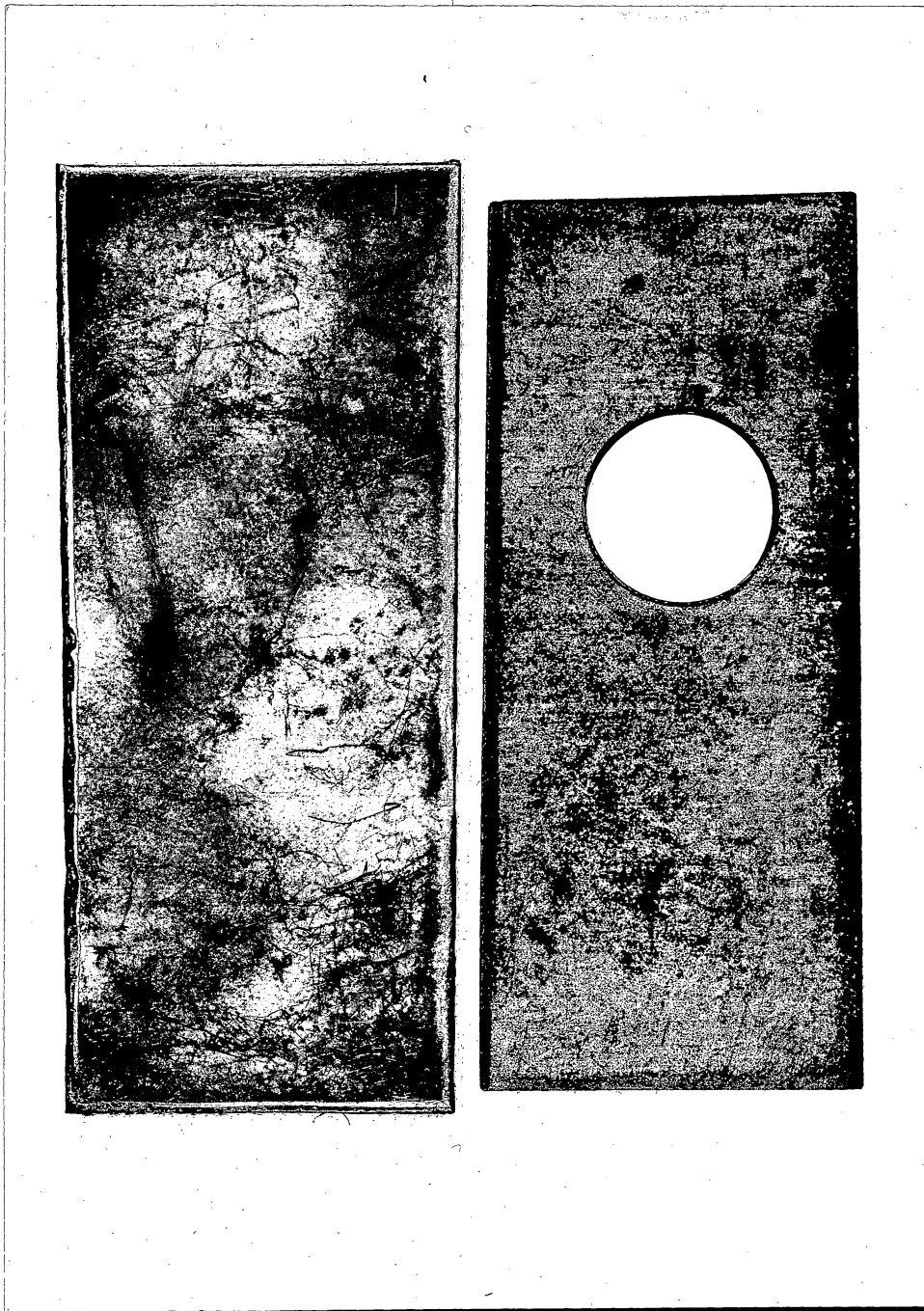


PLATE III
Corrosion Test Specimen

Left hand: Before exposure
Right hand: After exposure
Corroding agent: Crude fatty acids
Temperature: 570°-595° F
Time of exposure: 72 hours
Photograph: Two diameters
Composition of specimen: Cr: 16.69
Ni: 8.26
Fe: Balance

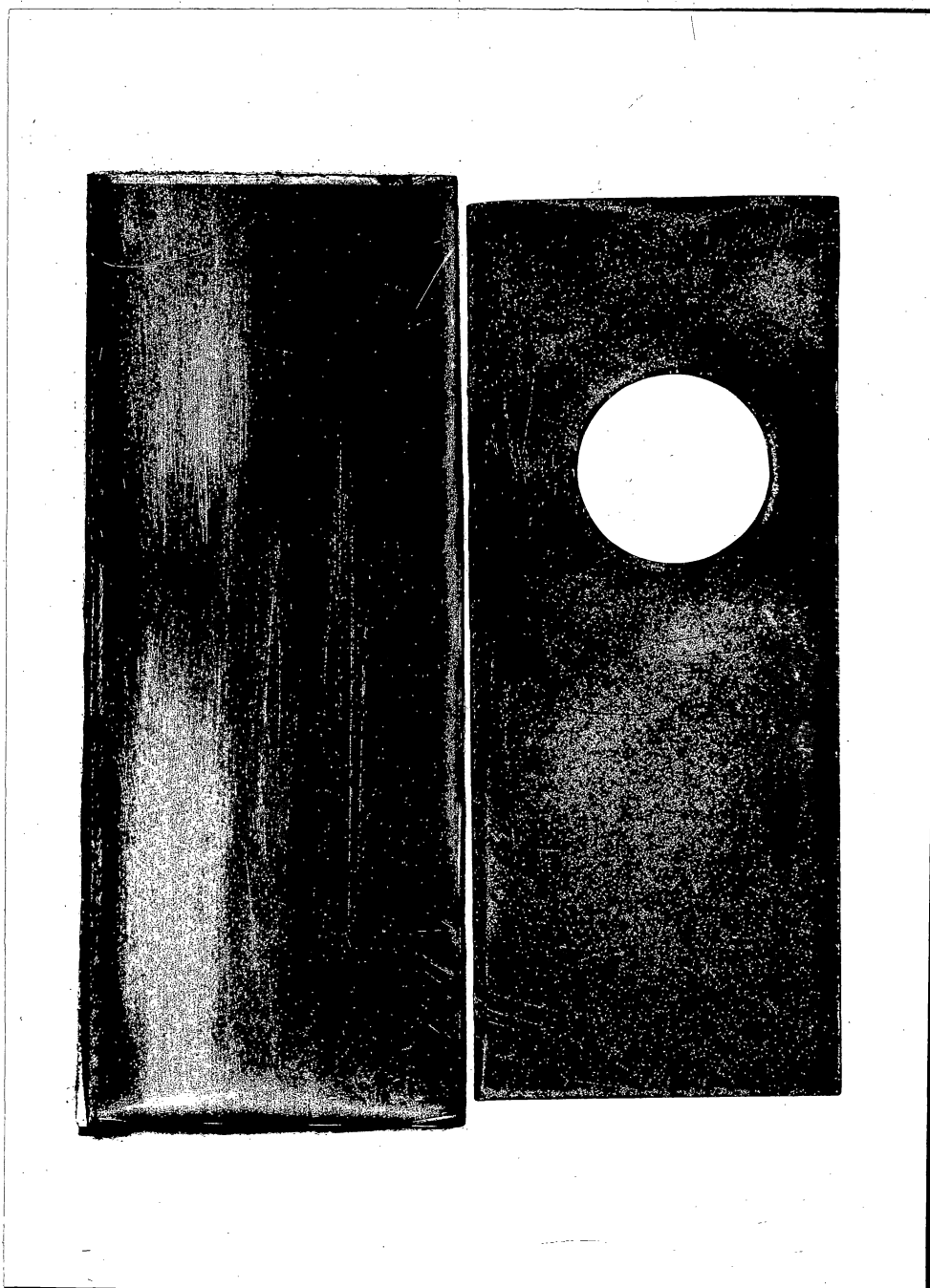


PLATE IV
Corrosion Test Specimen

Left hand: Before exposure
Right hand: After exposure
Corroding agent: Crude fatty acids
Temperature: 570°-595° F
Time of exposure: 72 hours
Photograph: Two diameters
Composition of specimen: Cr: 17.76
Ni: 8.75
Fe: Balance

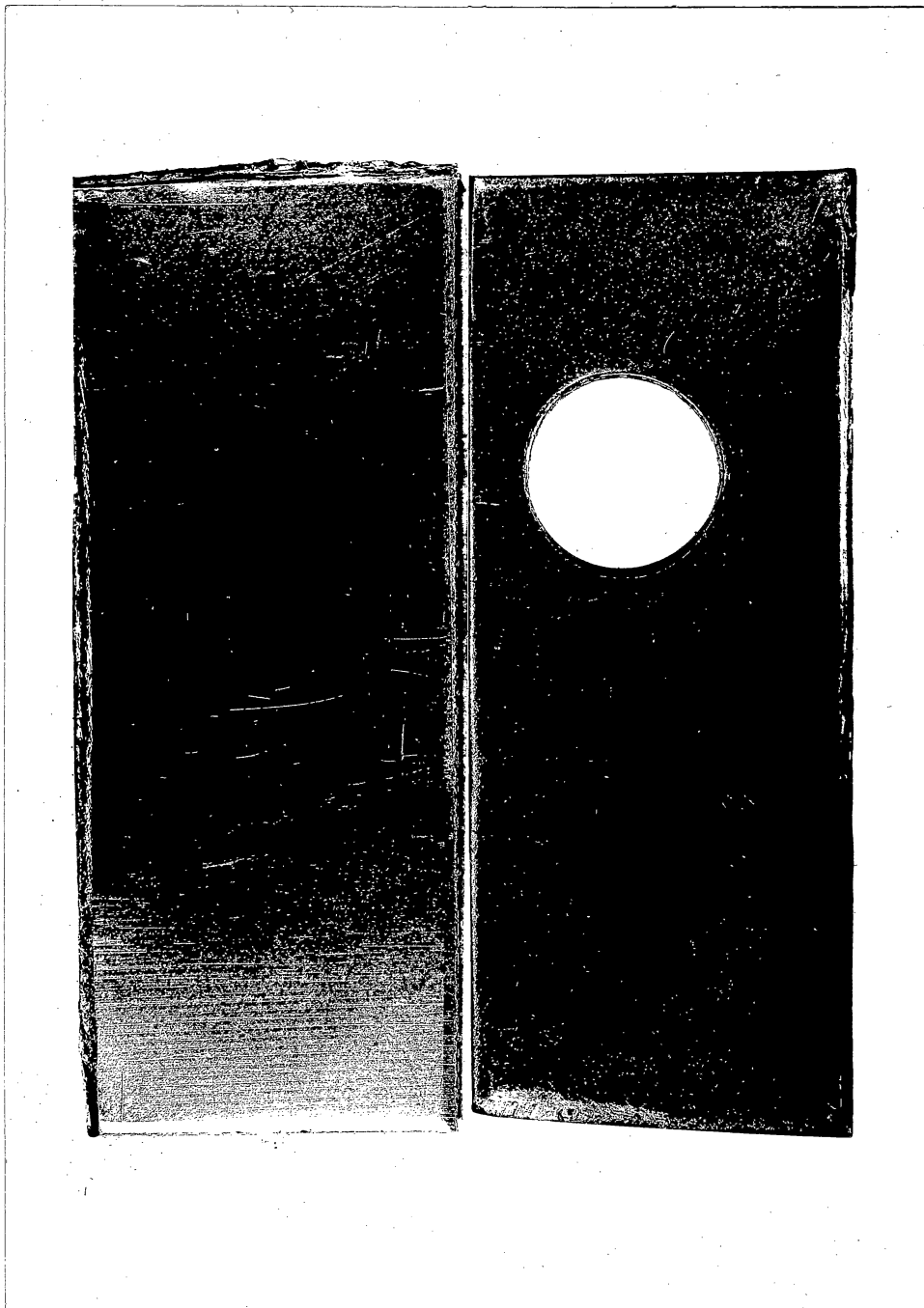


PLATE V

Corrosion Test Specimen

Left hand: Before exposure
Right hand: After exposure
Corroding agent: Crude fatty acids
Temperature: 570°-595° F
Time of exposure: 72 hours
Photograph: Two diameters
Composition of specimen: Cr: 17.7
Ni: 10.78
Mo: 2.34
Fe: Balance

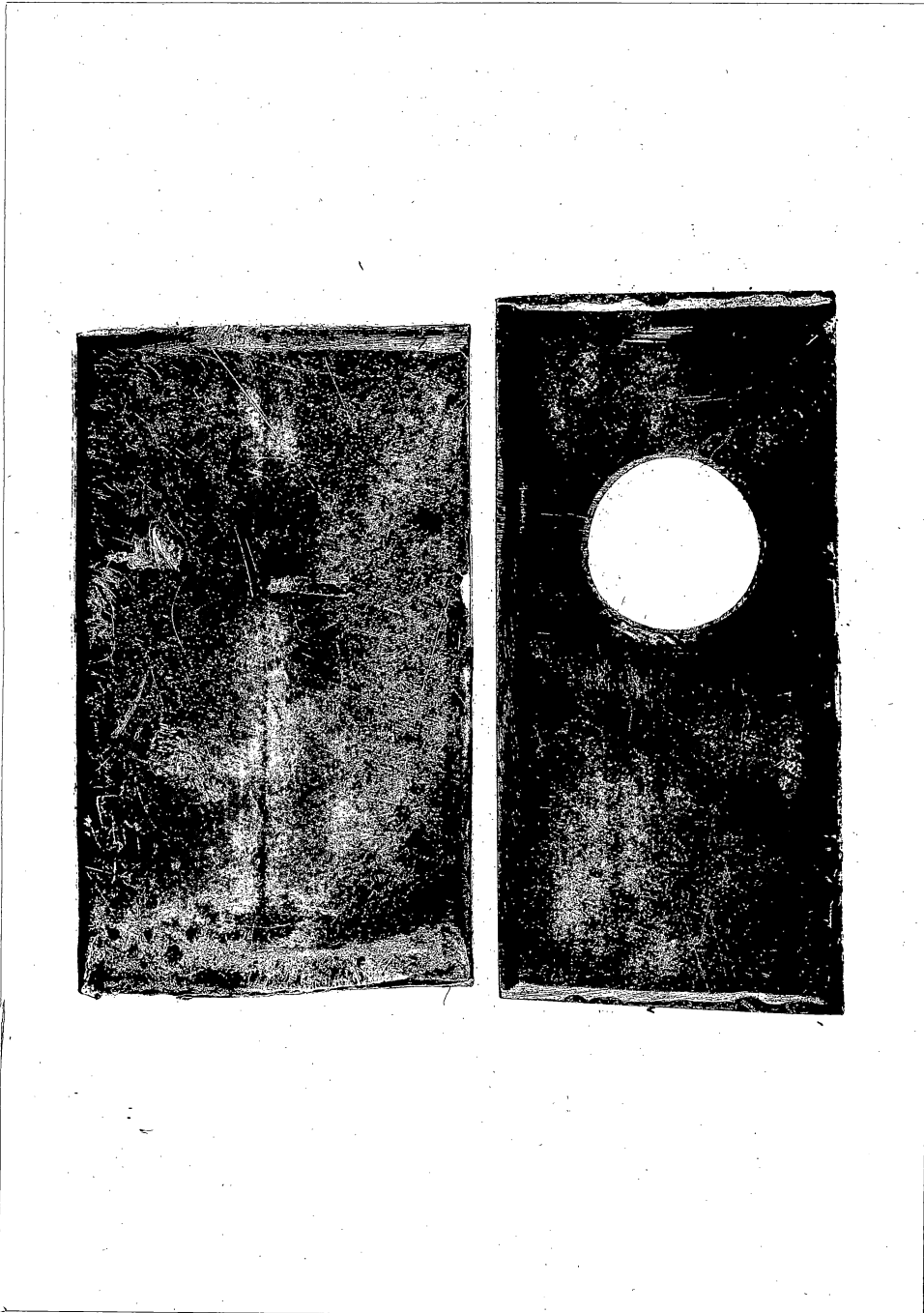


PLATE VI
Corrosion Test Specimen

Left hand: Before exposure
Right hand: After exposure
Corroding agent: Crude fatty acids
Temperature: 570°-595° F
Time of exposure: 72 hours
Photograph: Two diameters
Composition of specimen: Cr: 22.2
Ni: 10.4
Fe: Balance

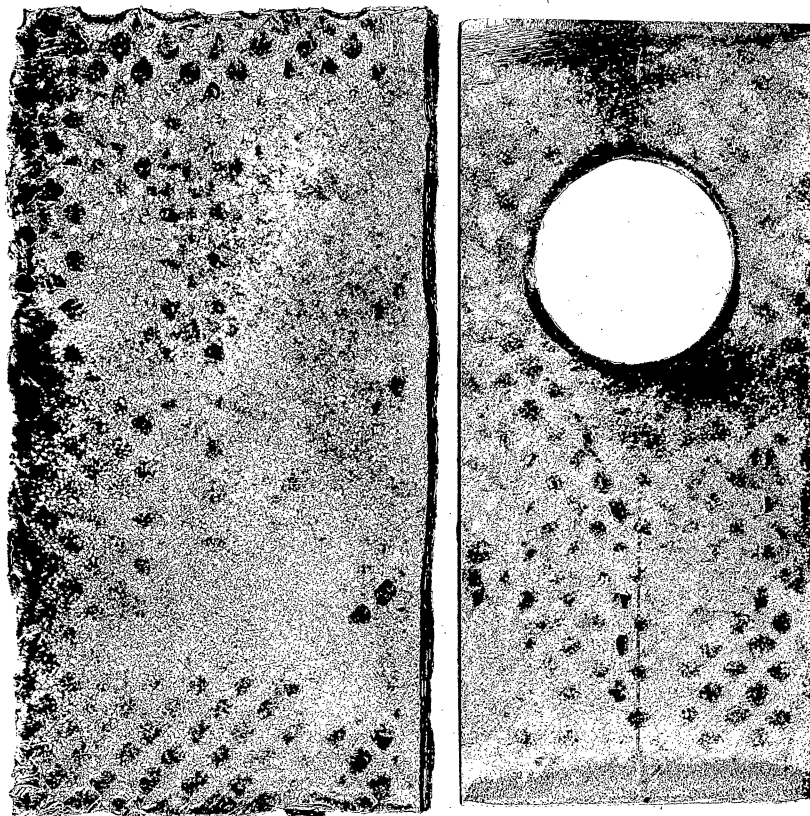
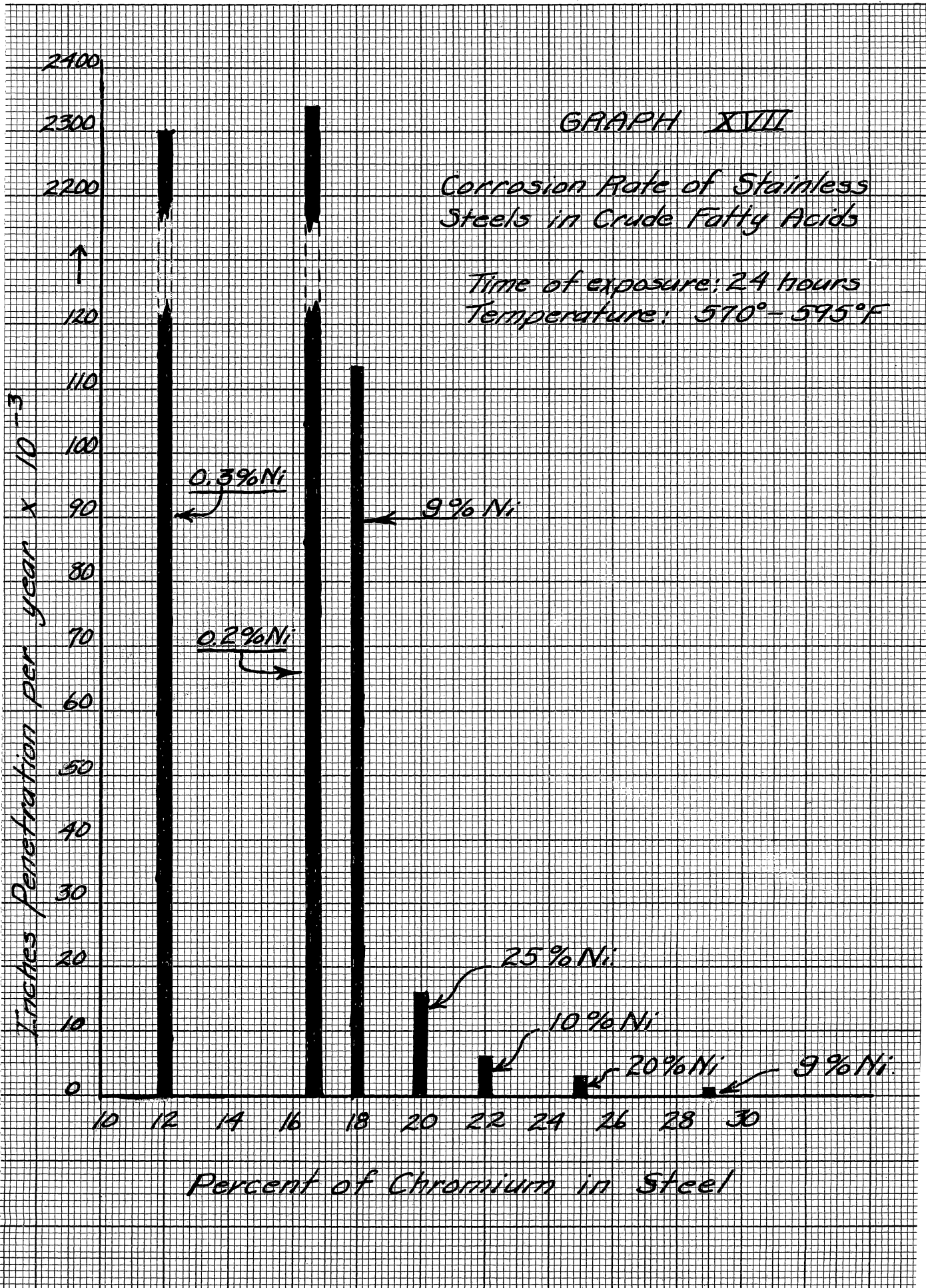


PLATE VII
Corrosion Test Specimen

Left hand: Before exposure
Right hand: After exposure
Corroding agent: Crude fatty acids.
Temperature: 570°-595° F
Time of exposure: 72 hours
Photograph: Two diameters
Composition of specimen: Cr: 25.2
Ni: 19.9
Fe: Balance



Discussion

Theory

Corrosion, in general, may be divided into two classes: first, direct chemical attack; second, electrochemical action. Examples of the first type are the action of dry chlorine, hydrogen, sulphide, or other gases on dry metals. The course and extent of such a reaction is dependent on the physical properties of the product, provided the energy relationship is such that the action takes place spontaneously. If the product is liquid or gaseous it will be continuously removed and the action will continue until the reactants are completely used up. On the other hand, if the product is solid and remains where it is formed, the film formed will hinder to some extent the action of the corrosive material on the metal. Such films as this have different characteristics, and if the film is porous it allows the corrosive agent to penetrate it and the corrosion continues but at a slower rate than formerly. However, if the film so formed is dense and impervious to the attacking agent, the metal will be protected.

It is interesting to note that a little over one hundred years ago Faraday (65) evolved the idea that a protective film of oxide was formed in order to explain the chemical passivity of iron to concentrated nitric acid. Due to the fact that this film was exceedingly thin and also invisible, the theory fell into disrepute for a long period of time, but researches in the last few years have definitely proved that such oxide films actually do exist, since they have been isolated and identified by Evens (63a) and other investigators.

Film on Stainless Steel

It is now a definitely accepted fact that the rust-resisting properties of the stainless steels are related directly to the properties of the invisible oxide film. Actually the film on the stainless steels is thinner than that on ordinary steel due to the fact that a truly protective film effectually hinders its own growth. The corrosion resistant properties of the stainless steels may be ascribed to the fact that the oxide film on the surface is automatically kept in repair by the action of the atmosphere. The same phenomenon is observed with chromium and aluminum.

Film Characteristics

Accepting then the fact that the corrosion resistance of the stainless steels is due to the repair of the oxide film by the atmosphere, the characteristics of the film in question should be determined for each specific case.

Hedges (66) states that "the protective power of a film is a relative term depending on all existing conditions, both physical and chemical," and "films of the oxide type are not resistant to wear, and unless they are automatically kept in repair, have only a limited use."

Effect of Cold Working

Evans (63) showed that the breakdown of the protective film on iron, steel, zinc, or aluminum tends to occur where the specimen has been bent or otherwise distorted with corrosion occurring preferentially at the bend. Breakdown of the film is also likely to occur where the surface has been cut or scratched. He emphasizes the fact that internal stresses are important in determining corrosion if they are of such a nature as to weaken the film. These conclusions are of great interest, since they throw new light on the preferential corrosion, or pitting of strained metal which has usually been

attributed to differences in electrolytic potential of adjacent sections of the metal due to the cold working of the metal; and they also suggest that part of the acceleration of corrosion by the presence of impurities in the metal may be due to the tendency of the protective film to fail at the phase boundary, especially as it has often been observed that inclusions of nonconducting materials form the focal point of accelerated attack and pitting.

Confirmation of Oxide Film

Johnston (67) states that the rate of reaction is the controlling factor in direct chemical attack, and that if this rate can be made substantially zero, the reaction will not proceed no matter how large the driving force. He continues, "it is now well known that the presence of chromium in steel lessens the rate of scaling to such an extent that the rate of scaling at 1200°C of a steel containing 27 per cent chromium is only about 1 per cent of that in the absence of chromium; but it is difficult to give an explanation for this behavior (for chromium is not a noble metal with respect to oxygen) except in general terms to the effect that chromium does form an oxide film which is adherent and highly impervious and can do this even when a majority of the atoms on the original surface are iron atoms. Apparently, however, the addition of chromium is much more effective in reducing scaling when at least 12 per cent is present; this corresponds to about one atom in eight by volume or one atom in two along any straight line on the surface. In other words, it would seem that every iron atom on the surface must be adjacent to a chromium atom if the latter is to be really effective in lowering the rate of scaling at high

temperature, and that further increase in chromium content beyond this point becomes more and more effective." He also states that the rate of scaling is proportional to the rate of diffusion of the oxygen through the oxide film, and if the oxide film is impervious to oxygen no further scaling or corrosion will occur.

This view is also held by Hedges (66), and is supported by the work of Pilling & Bedworth (70) and also by Evans (64).

From the evidence as presented it is reasonable to assume that an oxide film is present over the surface of the metals and that if this film is impervious to the corrosive agent no action will take place; and that if the film is only partially protective selective corrosion will take place at the weakest points, and this will be manifested by pitting.

Formation of Metallic Soap

Hedges (66) p. 11, defines corrosion by direct chemical attack as corrosion when no electrolyte is present. Since the crude fatty acids are non-conductors and the temperature at which the tests were carried out (580°F) precluded the presence of water, the corrosion takes place by direct chemical action.

Following the theory developed above, the action is controlled first by the diffusion of the fatty acids through the oxide film on the surface of the metals and following that by diffusion through the product of the reaction.

It was noted that for all samples that were appreciably corroded, a very sticky, but porous scale was formed that corresponded to that found in actual plant practice. From a purely physical examination it would seem

that this reaction product was a metallic salt of the fatty acids.

Classification of Metal Groups on Basis of Corrosion

For all the pure metals tested, with the single exception of Tantalum which was practically unaffected, the scale formed was very adherent to the surface of the metal. In the case of the low chromium nickel steels the scale was much more porous and easier to clean from the samples. For those samples that were not attacked to any marked extent, there was present only a trace of scale or none at all. From the above observations, the pure metals should be expected to fall between the low chromium nickel steels and the high chromium nickel steels in their resistance to corrosion, and an inspection of Table VII shows that this is indeed the case.

An examination of the results obtained from the tests shows that the chromium and nickel alloy steels show a complete range of resistances from the maximum to practically the minimum of any value found. Since these alloys from a commercial viewpoint are the most useful and since they have received more research attention than the others, this discussion will be concerned primarily with them.

Effect of Composition on Corrosion Rates

The remarkable fact unearthed in this research was the tremendous increase in resistance to corrosion from the 18-8 chromium nickel alloy to the 22-10 composition alloy. An examination of Table VIII shows that the corrosion rate decreases to approximately 1/12 of its former value by the slight change in composition, and microscopic examination of the specimen at 435 diameters showed no trace of scaling or pitting. It should be noted that the addition of approximately 3 per cent molybdenum to the 18-8 series also increases the corrosion resistance

to a value approximately equal to that of the 25-20 chromium nickel alloy. The addition of molybdenum to steels serves the same purpose as the addition of chromium, in increasing the strength or impenetrability of the oxide film. However, in the case of the chromium-nickel-molybdenum alloys it was noted that the finish of the specimen was tarnished to a considerable extent. Considering the short length of time that the samples were exposed to the corroding agent, it is doubtful whether the resistance to corrosion exhibited by these alloys would be as good as that of the chromium-nickel alloys of equal value when exposed over long periods of time. However, this remains to be proved by further research.

The Chromium-Nickel Content as Influencing Corrosion Rates

As previously noted, beginning with the 22-10 chromium nickel alloy and continuing up the series examination under a microscope at 435 diameters showed no trace of scaling or pitting.

This behavior of the metals can be accounted for very plausibly by the theory as developed. The samples having the least resistance to attack were those containing Cr 17.7, Ni 0.2 and Cr 12.7, Ni 0.3. For these alloys the oxide film was either discontinuous and non-protective or else somewhat porous so that the fatty acid diffused through it very readily and once the film was broken the corrosion proceeded apace since the fatty acids are very corrosive. The examination of the surface showed that corrosion was practically uniform over the entire surface of the specimen. There was marked pitting of the surface, but this was of the same relative magnitude over the entire specimen.

The next most resistant alloys were those of the so-called 17-7 and 18-8 compositions. These alloys showed deep pitting and selective attack wherever a file had scratched the surface in preparing the specimen and also

around the edges of the hole drilled in the specimen for the glass suspension rod. Much of the surface showed no marked signs of attack, but there were tiny pits more or less uniformly scattered over the entire surface. Scaling was present but not nearly so great as for the less resistant alloys. This would indicate that the oxide film was particularly weak in the spots where the metal had been cold worked and therefore very susceptible to attack at those points. Another logical deduction is that the oxide-forming tendencies of the chromium atoms present in the alloy were insufficient to completely protect the adjacent iron atoms over the entire surface and that the fatty acids diffused through the weak portion of the film at those points, thus beginning the attack.

The next alloy in resistance value had a composition of 22-10 chromium nickel and from microscopic examination showed no evidence whatsoever of either scaling or pitting. At 435 diameters it was impossible to detect any difference between the exposed and unexposed specimen. This would indicate then that sufficient chromium had been added to the alloy to permit the formation of an almost completely impervious oxide film over the entire surface of the alloy.

The final alloy of the series, having the composition 29-9 chromium nickel gave the best resistance value of the entire series and repeated immersions failed to produce any visible evidence of attack. In the case of this alloy the percentage of the alloying element has apparently reached a value such that the oxide film is for all practical purposes impervious to the action of the crude fatty acids.

Effect of Molybdenum on Chromium-Nickel Steels

The next alloy in resistance value was a so-called 18-8 chromium nickel, 3 molybdenum alloy. In this case no evidence of attack was apparent, but the

finish of the alloy was darkened considerably. An alloy of 25-20 chromium nickel and other 18-8 chromium nickel, 3 molybdenum alloy showed somewhat the same resistance value and should probably be grouped together. Again no surface evidence of corrosion was apparent for all of the above-mentioned alloys.

Effect of Silicon Content on Chromium-Nickel Steels

Samples #11 and #15 in Table VII are apparently out of place in the chromium-nickel resistance series. However, these are special alloys containing appreciable amounts of silicon, and this fact should account for their slightly decreased resistance. Sample #19 shows too high a resistance according to the chromium nickel resistance series and may be accounted for by the fact that its surface was very rough and difficult to clean free of fatty acids and a slight gain in weight from such a cause would account for its apparent increased resistance. The same reasoning applies to the high silicon iron, sample #23, since it is believed that this is also slightly out of place.

Effect of Other Metals on Corrosion Rates

I. Cast Iron. Referring to Table VII to evaluate the other specimens of metals and alloys tested, it is found that the following is true. Sample #3 was a sample of cast iron containing small percentages of Cu and Cr. The corrosion rate on this was so rapid as to leave no doubt of its unsuitability.

II. Aluminum. Aluminum and its alloys are next in line in order of increasing resistance to corrosion, and their rate and scaling preclude any use against crude fatty acids. However, one fact was noted in the case of these samples that should be mentioned; they were the only samples tested that showed an increase in corrosion rate during the second period of immersion. This is to be expected though, since aluminum is a very reactive

metal and depends entirely upon its oxide film for protection. Once this film is weakened or broken the reaction should proceed very rapidly, as it apparently does.

III. Copper. Copper apparently formed a very adherent scale upon reaction with the fatty acids, and the rate of corrosion is probably dependent upon the removal of this scale. In a pipe still with high velocities of the corroding material, this rate would probably be much larger. Pitting was also apparent.

IV. Nickel. Nickel is apparently the most resistant of the pure metals of construction, but it too has the disadvantage of scale formation, although pitting was very slight.

V. Tantalum. Tantalum was apparently unattacked but cannot be considered for any industrial application since the operating temperatures are so close to the temperature at which it is embrittled. Fabrication difficulties would also preclude the use of the high silicon iron except for auxiliary equipment. Further test should be run on smooth finished samples of this material before any reliability can be placed on the test data.

In the test runs as performed it was attempted to duplicate as near as possible conditions that would be encountered in actual plant practice. However, there are certain facts which must be considered before any but a relative interpretation can be placed upon the results. The first and most important of these considerations is that the fatty acids were continuously decomposed during the course of the runs by destructive distillation. This is evidenced by the drop in the acid value of the crude fatty acids during the course of each test. This of course would indicate that the corrosion rates as shown are of a lower value than would be

expected in plant practice where the metals would be continuously subjected to the action of fresh material. The other factor, and one that is much more difficult to evaluate, is the effect of heat transmission through the metal itself as would be the case in actual practice. In the case of the test runs heat was supplied to the specimen from the fatty acid itself. This may or may not have an effect on the corrosion rate and will probably have to await further research for an actual decision, but should be remembered in any case.

The volume of fatty acids used for the tests was very large (two gallons) in comparison to the size of the specimens of metals. Therefore it is reasonable to assume that the quantity of fatty acids consumed by reaction with the metals to produce a metallic soap was negligible.

CONCLUSIONS

From the evidence as presented, the following conclusions are possible:

1. Copper, nickel, aluminum, and their alloys have corrosion rates too high to permit their use as a material of construction for stills.

2. Stainless steels up to and including 18-8 chromium nickel content are entirely unsatisfactory in their corrosion resistant properties.

3. 18-8 chromium nickel stainless steels with approximately 3% molybdenum added are satisfactory in their resistance.

4. Stainless steels with a minimum nickel content of 8% and a minimum chromium content of 22% are satisfactory, and increasing the chromium content above that percentage increases the resistance of the alloy to corrosive attack by crude fatty acids. The choice of the particular alloy composition will depend on economic factors.

5. It is indicated that the resistance of the high chromium stainless steels is due to the property of chromium of forming an oxide film over the surface of the alloy that is impervious to the action of crude fatty acids. The protective quality of this film is probably dependent upon the distance between the chromium atoms on the surface.

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SUMMARY

This investigation was undertaken in order to determine the characteristics of crude fatty acids, recovered from the resin soap wastes of kraft pulp manufacture, so that efficient distillation units may be designed for distillation of the crude fatty acids.

It was found that the crude fatty acids could be distilled at a maximum absolute pressure of 7 m.m., and at a temperature range of 400° to 520° F. At this temperature range approximately 70% of the total can be recovered as distillate ~~pitch~~ without impairing the quality of the distillate. The remaining 30% is removed as pitch.

It was found that when 70% of the total has been distilled approximately 85% of the fatty acids and 80% of the abietic acid originally present have been recovered.

Crude fatty acids corroded to a marked extent all of the feasible alloys and metals of construction with the exception of the stainless steel containing not less than 20% chromium and not less than 9% nickel.

It was found that the most suitable alloy was a chromium-nickel-iron alloy containing 29% chromium and 9% nickel, the balance being iron.