UNCLASSIFIED

NYO-5094

CHANGES IN EXTRACTORS

TO PREVENT EMULSIONS

23 001

MALLINCKRODT CHEMICAL WORKS
Harold Yeager

Contract No. W-7405-eng-1
March 27, 1945

Photostat Price $ 7.80

Microfilm Price $ 3.30

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

UNCLASSIFIED

CLASSIFICATION CANCELLED

DATE MAR 8 1957

For The Atomic Energy Commission

Chief, Declassification Branch

Chemists and Chemical Engineers

Harold Yeager

J. A. Kyger

Howard L. Wibbels

W. C. Rosenbaum

R. R. Midlam

H. V. Farr

C. D. Harrington

H. E. Thayer

Glass Blowing was done by W. Hilker

Photography was done by David Copenhafer

I. Introduction

In the ether extraction step of the Chemical 306 process, considerable loss in production has resulted because of "emulsions" in the extractor. In this report, an "emulsion" will be defined as a mixture of ether and water solution of "hex" ($XO_2.(NO_3)_2.6H_2O$) which has been formed in such a manner that the ether layer and water layer are not readily separable.

Because the chemical methods of treatment to prevent emulsion--water leach, acid leach, and Tank 7 treatment--were not always completely satisfactory, and also because of a number of observations made in the plant extractors and a small laboratory model extractor, it was decided to try to find some mechanical method of prevention of emulsions.

II. Object

It was desired to run a series of laboratory extractions to indicate the necessary changes to be made in the plant extractors so that emulsions would not be formed.

III. Summary of Work Done

Several experiments were run in the laboratory to determine the best proposed change in the plant extractors. At the completion of the experimental program, plans were drawn and the desired changes were made. After the extractors were changed to prevent emulsions, data was accumulated to determine the effect in efficiency of extraction, efficiency of washing, and the increase in production.

IV. Historical Background

A. Chemical Treatments to Prevent Emulsions

Although occasional emulsions were formed in the extractors while working the N.G. liquor from the old type black oxide (X_3O_8), no serious loss in production was caused by emulsions until sodium salt was used in the Chemical 306 process. Hence, a large amount of research was done to find methods of treating

023 003

both crude material and in process N.G. liquors to prevent emulsions. For N.G. liquors (except N.G. 1 and N.G. 2), the following plant procedure was followed: The liquor was diluted with tap water to a Baume less than 43° and heated to a temperature of 170-180°F. A 20°Be solution of caustic was added to the liquor until a pH of 2.3±.1 was attained. (At this pH the $XO_2(NO_3)_2 \cdot 6H_2O$ is still soluble, but less soluble materials, such as phosphates, iron, etc., will precipitate.) The liquor was then filtered. The filtrate was then precipitated with caustic to form an insoluble sodium salt which contained approximately 3% Na and 70-75% X. This treatment is still used on all N.G. 3 liquor and all sodium salt liquors which have been extracted twice.

For crude material, three different treatments were used to try to prevent emulsions: (1) acid leach to remove excessive sodium (> 3%) from the salt, (2) barium carbonate treatment to remove excessive sulfate (> .2%), and (3) the N.G. treatment described above on the dissolved liquor from the sodium salt.

The acid leach to remove sodium was accomplished by adding nitric acid to a slurry of sodium salt and water at 150-170°F until a pH of 3.0-3.5 was attained. Caustic was then added to the slurry until a pH of 5.0-6.5 was attained, at which point the slurry was filtered and washed to remove the excessive sodium. Although the emulsion problem could not be attributed to the excessive quantity of sodium in the salt, this acid leach did help considerably in the prevention of emulsions.

The barium carbonate treatment was accomplished by adding barium carbonate to a nitric acid solution of sodium salt and boiling the liquor to precipitate the sulfate as $BaSO_4$. The $BaSO_4$ was then filtered from the slurry. The precipitation of sulfate as $BaSO_4$ was not complete in the nitric acid solution, but considerable quantities of sulfate could be removed by this procedure.

B. Methods of Breaking Emulsion in Plant Extractors

When emulsions were formed in the extractors, the operators used several methods for breaking the emulsion. These three methods are: (1) recycling, (2) adding ether, and (3) adding water.

The method which was found to be most reliable was recycling. To break an emulsion by recycling, the operator would recycle the material in the extractor for 2-5 minutes and then allow the mixture to settle for about ten minutes, at which time he would drain the amount of water layer which had separated. He would then repeat the operation of recycling, settling, and draining until no emulsion appeared above the water layer. This method of breaking an emulsion would require a period of time of from ten minutes to eight hours, though the usual time required was about thirty minutes.

Another method of breaking emulsions which sometimes worked was the addition of about twenty-five gallons of ether to the extractor and then subsequent recycling and settling. This method of breaking emulsions was found to be quite helpful in cases where recycling and settling alone would not break the emulsion.

Another method of breaking emulsions was the addition of quantities of water varying from ten gallons to fifty gallons and then subsequent recycling and settling. This method of breaking an emulsion was usually the fastest method if it worked; however, in many cases when water was added to the extractor to break an emulsion, the emulsion would become much worse.

The three methods for breaking emulsions mentioned above were the general methods used; however, each operator was the sole judge as to which method would be best. Also, each operator would use his own particular variation of the general methods to break the emulsions.

C. Control Extraction Tests

In the period from the latter part of 1942 to the latter part of 1943, all sodium salt was tested by an extraction test before the salt was consumed by the plant. This extraction test was performed in an open conical glass in which proportionate amounts of "hex" from the salt and ether were mixed with a glass stirrer which was powered by a small air motor. However, the extraction test was very inadequate because material which gave a good extraction test might easily form an emulsion in the plant and, on the other hand, material which failed the extraction test would often be extracted very easily in the plant extractors. This variation was attributed to the fact that the method of mixing in the laboratory was not similar to the method of mixing in the plant.

In order to obtain a set-up similar to the plant extractor, a glass extractor was designed by Harold Yeager and Dr. J. A. Kyger.* This extractor set-up is shown in its final form by Illustration I. The original set-up may be visualized by eliminating lines D, C, H, and F and stop-cock 3. The capacity of the extractor is 1500 cc. Stop-cock 1 on line A represents the bottom outlet of the plant extractor. Line B represents the sight-glass on the extractor. Valve 5 represents the valves used for draining N.G. and O.K. liquor from the extractor. The liquor is recycled by a small Eastern pump which is powered by an air motor. The liquor is cooled while recirculating through a single-pass heat exchanger. Stop-cock 8 is used for draining and washing the extractor after a run has been completed. "Hex" is added by gravity through line G from a separatory funnel. The ether is condensed and re-fluxed into the extractor from the spiral condenser. Both the heat-exchanger and the condenser are cooled by circulating ice water.

An attempt was then made to use this extractor set-up for the extraction test. However, this method for the extraction test was not entirely satisfactory, because material which would form an emulsion in a laboratory extractor would sometimes give very little trouble in the plant; but material which did not form an emulsion in the laboratory extractor would run very well in the plant extractor.

---

*All of the glass blowing on this job was done by Mr. William Hilker.

D. Preliminary Experiments in Glass Extractor

Although the model extractor was rather unsuccessful as a control tester for plant material, a number of runs were made in the extractor to study the actual conditions which existed in the extractors while emulsions were being formed and also while they were being broken by the usual plant methods. It was during two of these random experiments that observations were made which led to other experiments which were successful in breaking emulsions.

During one random run in the model extractor, a very thick emulsion was formed which filled about two-thirds of the extractor. This emulsion was recycled for about ten minutes and the amount of emulsion was not increased nor was its emulsifying property decreased. An attempt was then made to fill the extractor with emulsion. To do this, the emulsion layer was drained and the ether was recycled while the emulsion was slowly added to the extractor. As soon as all of the emulsion had been returned to the extractor, the pump was stopped and the mixture was settled. Instead of filling the extractor full of emulsion by this method, the emulsion was entirely broken and a complete separation of the ether layer and the water layer was attained.

During another run, an attempt was made to study the breaking of an emulsion by the recycling method. After the emulsion had been recycled, settled, and drained two times, the emulsion had been reduced to the point where the emulsion layer was not as high as the upper inlet to the sight-glass. When the pump was started again for recycling the emulsion, the pump began pumping a large amount of the ether layer through the sight-glass and only a small amount of emulsion through the bottom outlet. The mixture leaving the pump was a finely dispersed, free-flowing mixture of ether and water solutions instead of the viscous emulsion which had been pumped in the previous recycling operations. The emulsion was gradually drawn from the bottom and dispersed into the ether layer until all of the emulsion had disappeared. The pump was then stopped, and a complete separation was attained in less than two minutes.

023 007

These two accidental experiments led to the first change in the model extractor in which a side outlet was installed near the top of the extractor so that the ether layer in the extractor could be drawn into the pump simultaneously with the emulsion layer at the bottom of the extractor.

V. Emulsion-Breaking Experiments

A. Extractor Set-Up I

The extractor set-up for the first experiment may be visualized from Illustration I by eliminating lines C, H, F, and stop-cock 3.

A typical run with this set-up is shown in Illustrations II, III, IV, V, and VI. In these photographs, however, line C is used to break the emulsion instead of line D, which was originally used, because the bottom outlet of line C is located at the point where the outlet of line D was located for this set-up.

Typical data for a run with this set-up would be as follows:

Volume of ether at start of run	850 cc
Volume of "hex" to be added	500 cc
Temperature of ether at start of run	10°C
Temperature of "hex" to be added	70°C
Temperature of mixture after "hex" solution	35°C
Time required for "hex" addition	15 min.
Amount of "hex" added when emulsion starts forming	150 cc
Volume of water layer separated after four minutes settling	150 cc
Volume of emulsion after four minutes settling	550 cc
Volume of ether layer after four minutes settling	550 cc
Time required to break emulsion	5 min.
Volume of water layer after four minutes settling (emulsion broken)	300 cc
Volume of ether layer after four minutes settling (emulsion broken)	950 cc

023 008

ILLUSTRATION I

023 009

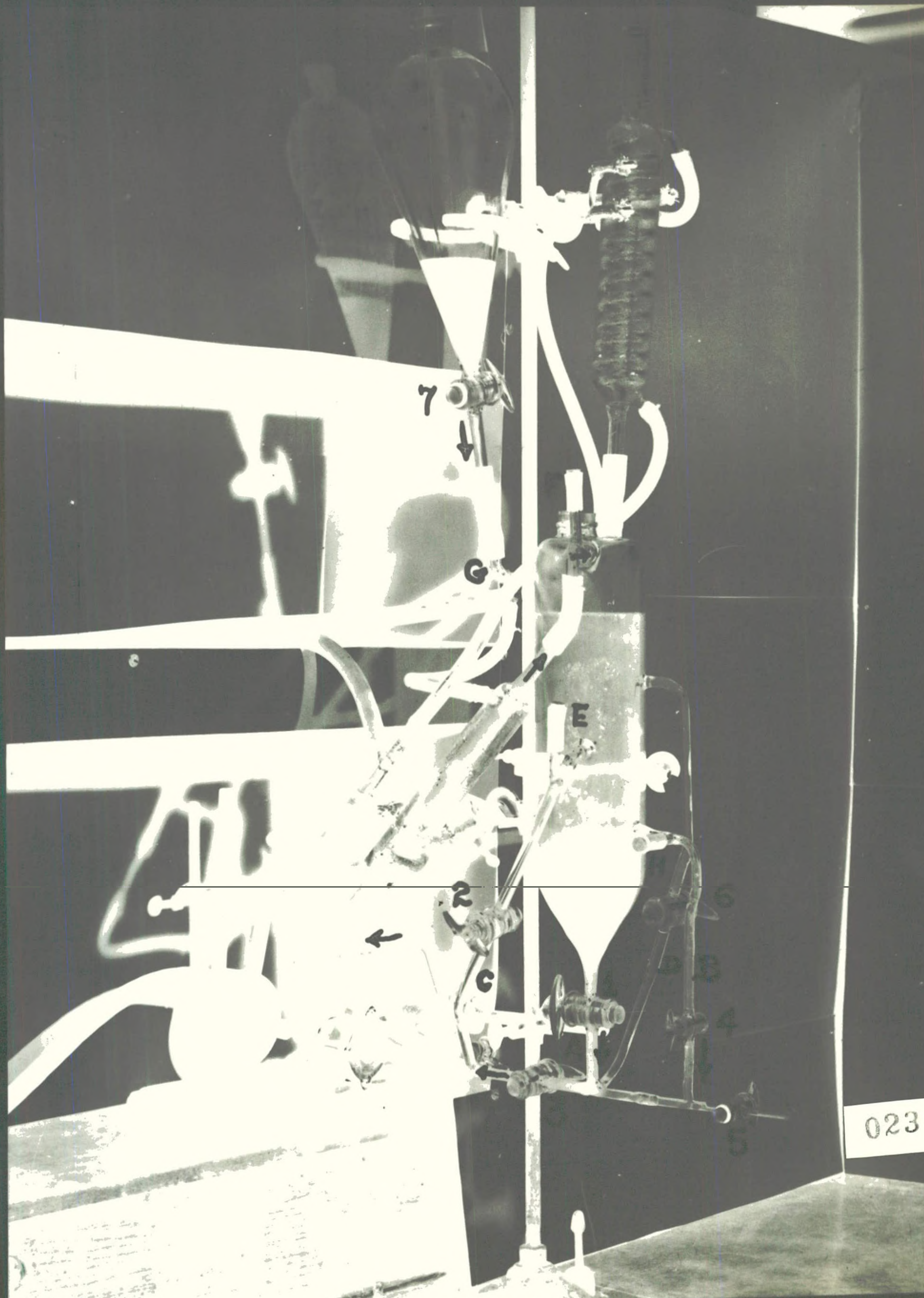


ILLUSTRATION II
ADDITION OF "HEX" FROM CHEMICAL 182

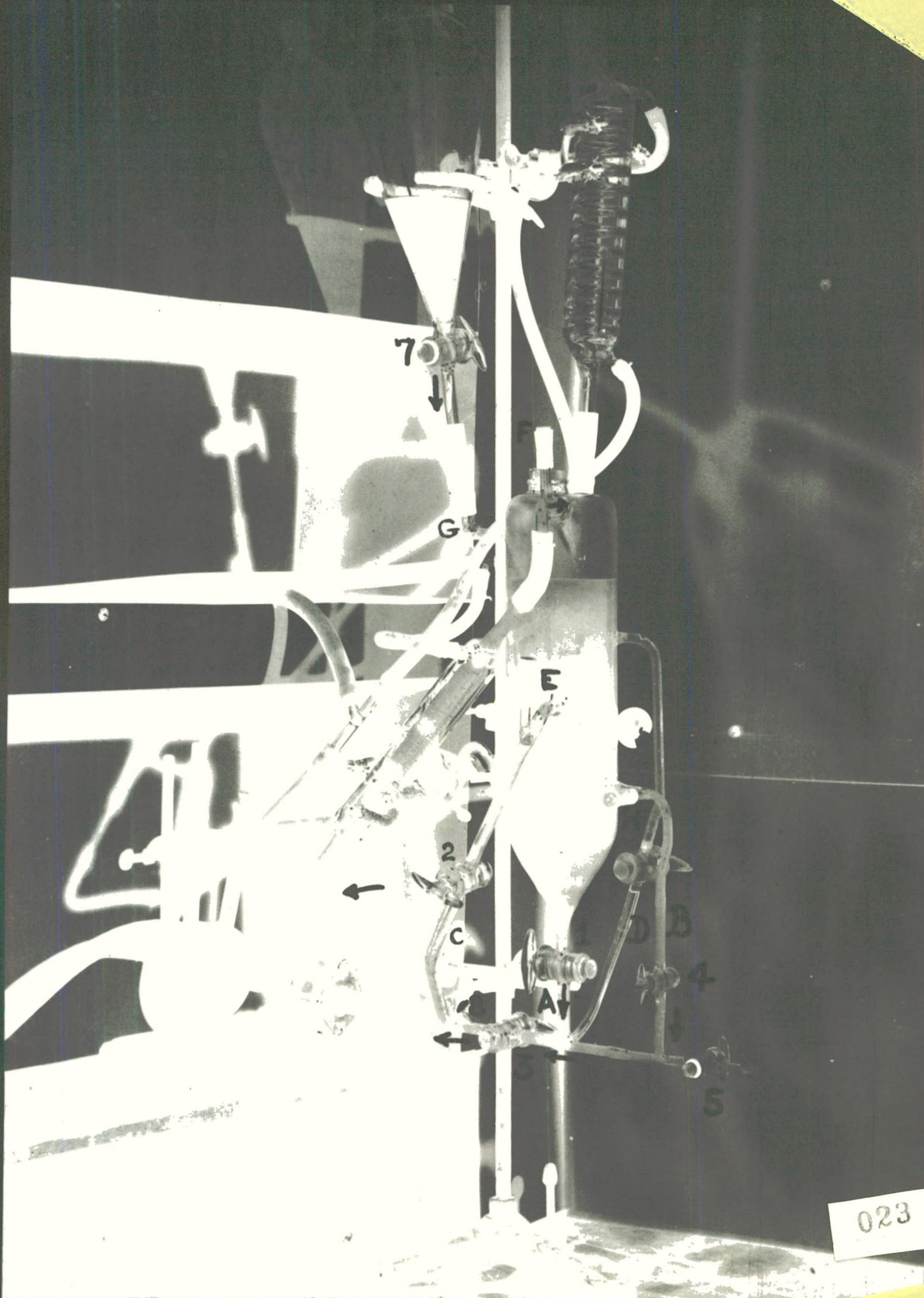


ILLUSTRATION III
ADDITION OF "HEX" FROM CHEMICAL S
(EMULSION FORMING)

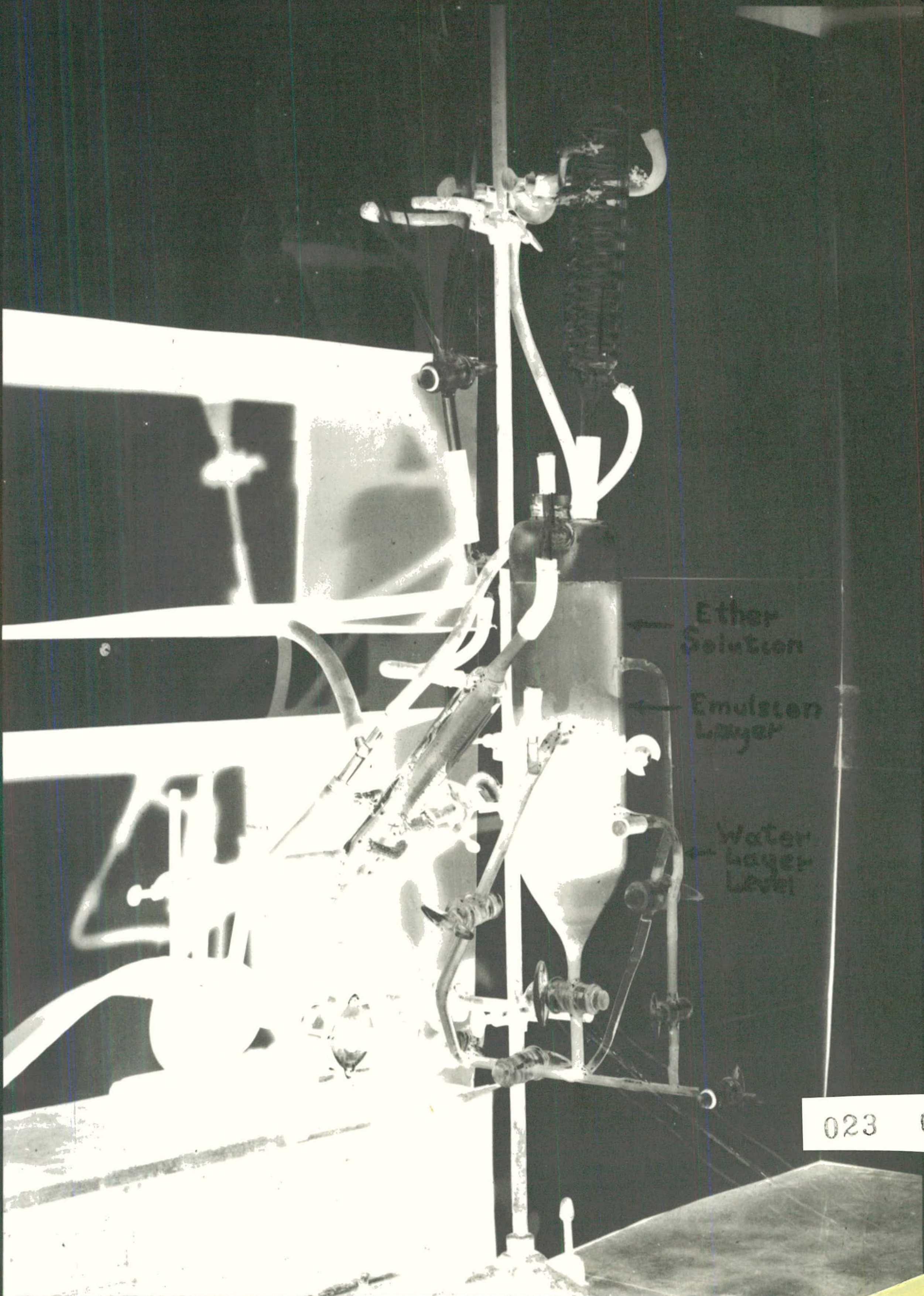
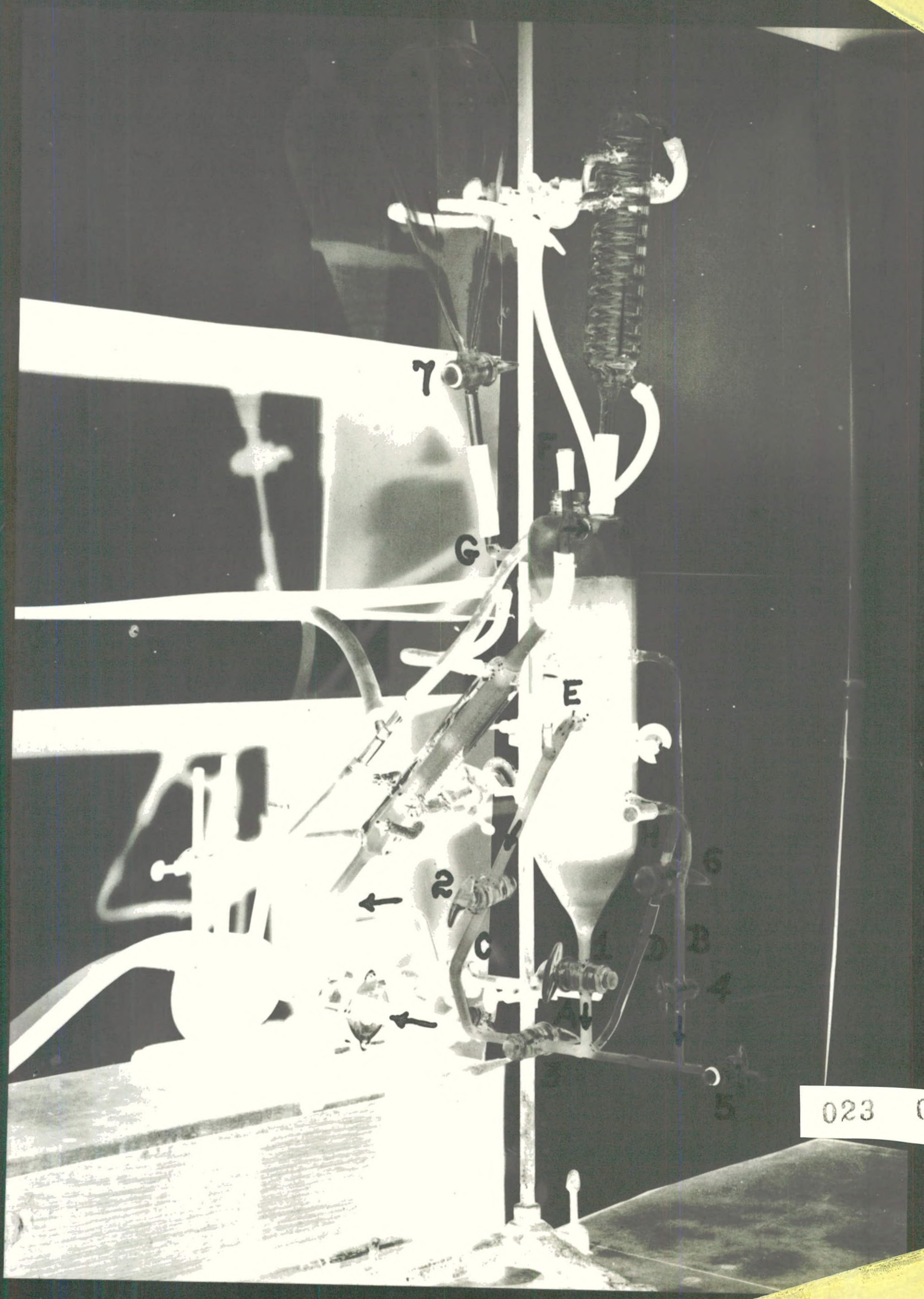


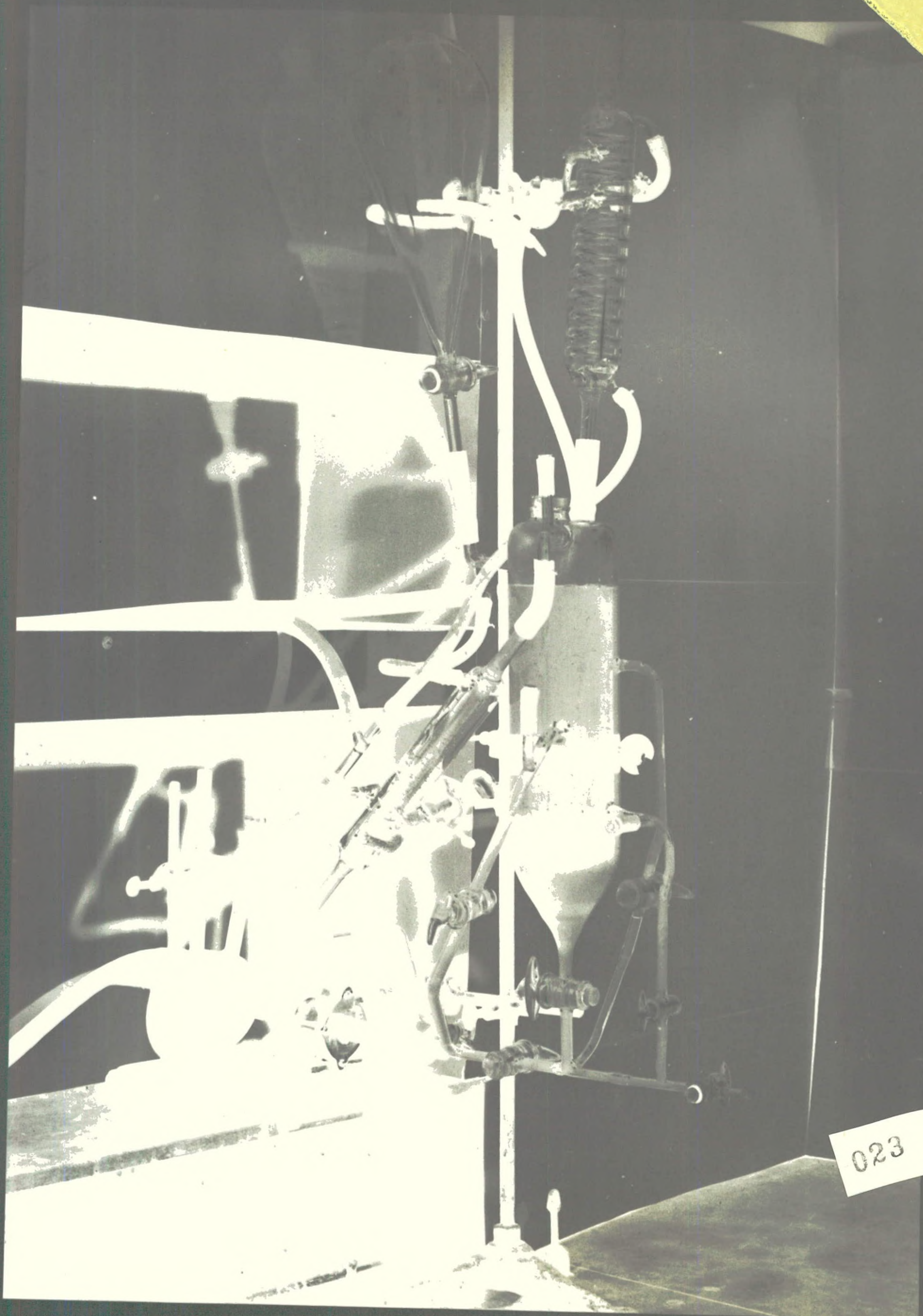
ILLUSTRATION IV
EMULSION FROM CHEMICAL S

023 012



023 013

ILLUSTRATION V
BREAKING AN EMULSION



023 014

ILLUSTRATION VI
COMPLETE SEPARATION OF ETHER AND WATER LAYERS

DECLASSIFIED

Illustration III shows the condition in the extractor after about two-thirds of the "hex" has been added. "Hex" is being added through line G and the mixture is being circulated from lines A and B through the heat exchanger into the top of the extractor.

As the liquor is being recycled, it will be noticed that complete mixing is not being attained in the extractor. The upper one-third of the extractor contains relatively clear ether, whereas the lower two-thirds of the extractor contains the emulsion which is continuously being recirculated. While the emulsion is being recirculated, the liquid coming back into the extractor is a heavy viscous liquid which immediately falls through the ether layer.

Illustration IV shows the condition in the extractor after all the "hex" has been added and the mixture has settled for four minutes. At this time the water layer, which can be seen in the sight-glass, was rising very slowly. In ordinary plant practice for this type of emulsion, this water layer would be drained and the remaining contents of the extractor would be circulated.

Illustration V shows the liquor circulating as the emulsion is being broken. To break the emulsion, stop-cocks 1 and 4 were closed and stop-cock 2 was opened. The pump was started and, as soon as the line leading to the pump had been filled with ether instead of emulsion, stop-cock 1 was opened about half way and stop-cock 4 was completely opened. Under these conditions, the emulsion layer will gradually drop and emulsion is dispersed into the ether layer. By inspecting Illustration V, the reader will notice that lines C and B have a light colored liquid in them, whereas line A contains the dark emulsion; there is complete mixing of the ether and water at the top of the extractor, which did not occur as "hex" was being added to the extractor. As soon as the liquid going through line A is the same as the liquid going through line B and C, the emulsion will be broken.

Illustration VI shows the complete separation attained in a two-minute settling period after the emulsion was broken. Comparison of Illustration VI with Illustration IV will give the reader an idea of the amount of the ether which would be lost if the emulsion could not be broken.

After an emulsion was broken in the extractor, it could easily be formed again by merely adjusting the stop-cocks in such a manner that the ratio of the volume of water layer to the volume of the ether layer entering the pump is increased to the point where an emulsion will be formed in the pump.

Numerous runs similar to the run shown in the photographs were made using all the types of liquor which were used in the plant. In every case where an emulsion was formed, the method described above was found to be successful in breaking the emulsion. The laboratory model worked very well, but one of the major objections to using this set-up in the plant was that the plant extractors are of stainless steel construction and the operator can judge the condition in the extractor only by the sight-glass. While it may not be necessary for the operator to see the emulsion in order to break it with a set-up similar to Set-up I, it is certain that the breaking of an emulsion by this method in the plant would be more difficult to do than the breaking of the same emulsion in the glass extractor.

3. Extractor Set-up II

At the time when an alteration in the plant extractor similar to Extractor Set-up I was discussed, it was decided that the alterations could be more easily made if the emulsion breaking line could be connected at the T which the pump intake line made with the drain line on the extractor; otherwise, in order to get the emulsion breaking line in between the pump inlet and the extractor drain, the pump would have to be moved back. Hence, line outlet on line D was moved to the position as is shown in Illustration I.

A number of runs were made with extractor set-up similar to the runs made in Extractor Set-up I. In all of these runs the data obtained was similar to data obtained in Extractor Set-up I, escept that the period of time required to break the emulsion was usually longer and also the adjustment of the stop-cocks to obtain favorable ratios of ether and water layers going into the pump was considerably more difficult.

023 016

C. Extractor Set-up III

Because there was some doubt as to the ability of Set-up I or Set-up II to work in the plant, it was decided to attempt to find a way of preventing the formation of emulsions in the plant.

All of the runs in the glass extractor had indicated that the cause of emulsions was an improper ratio of water layer to ether layer entering the pump. It is obvious from the runs in Set-up I that the ratio of 1.7 ether volume to 1 water volume is satisfactory because the ether layer and water layer were entirely mixed and no emulsion was forming in the pump. It was suggested by H. L. Wibbels that the "hex" could be mixed with the ether before it entered the extractor by introducing it in the return line from the pump. It was thought that the "hex" would be dispersed in the ether layer and not allow an unfavorable rate of water layer to enter the pump.

This extractor set-up is shown in Illustration VII as "hex" is being added to the extractor through line F. For this set-up, lines C, D, H, E, and G were not used. In the illustration shown, no emulsion had begun to form, whereas, if the "hex" had been added through line G instead of line F, an emulsion would have started to form. Using this set-up, however, an emulsion usually started forming about the time one-half of the "hex" had been added.

While this set-up was not successful in preventing emulsions, it was a step in the right direction; and it also helped eliminate the problem of vapor locks in the pump while "hex" is being added.

D. Extractor Set-up IV

One of the reasons for Extractor Set-up III not working was believed to be inefficient mixing of the ether layer and "hex" added. It was noticed in the runs with the previous set-up that the emulsion started forming at the time when a water layer began to settle out in the lower part of the

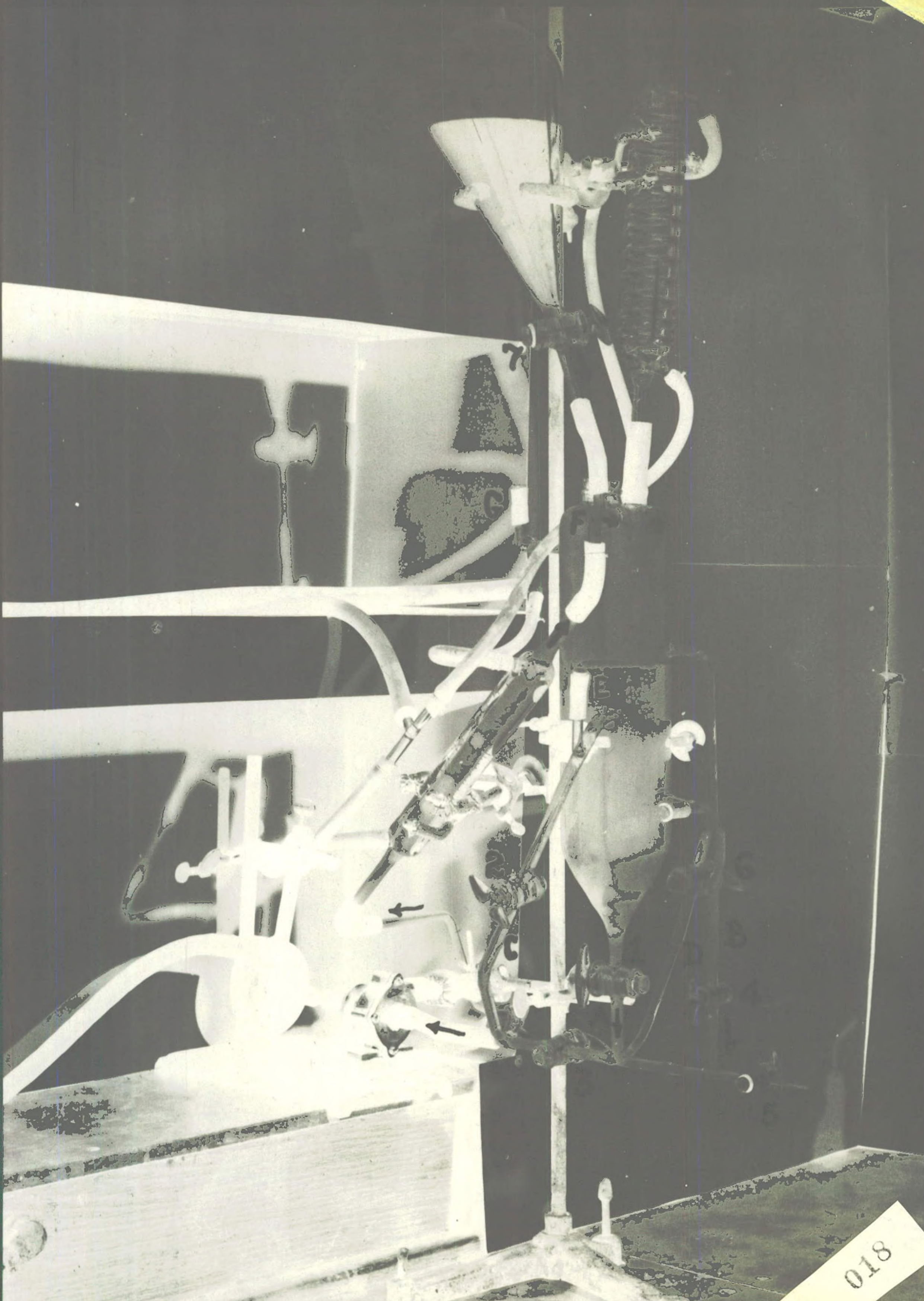


ILLUSTRATION VII
ADDITION OF "HEX" FROM CHEMICAL S
EXTRACTOR SET-UP III

DECLASSIFIED

023 018

extractor. Hence, it was believed that with thorough mixing of the ether circulating with the "hex" coming into the circulating line, the water layer would be finely dispersed in the ether layer and would not settle until the pump was stopped.

Hence, a centrifugal pump was placed in the return line between the extractor inlet and the point where "hex" is added. This set-up is shown in Illustration VIII.

Illustration VIII shows the "hex" being added through line L. Liquor from the extractor is circulating from lines A and B through the two pumps back into the top of the extractor. In this illustration, about one-half of the "hex" has been added and no emulsion had begun to form.

Two runs were made with this set-up using "hex" liquor from two different types of sodium salt. In both runs 500 cc of "hex" was added to 850 cc of ether. In the first run, the "hex" was added over a period of 20 minutes. No emulsion formed until about 10 cc of "hex" was left to be added. In the second run the "hex" was added over a period of time of fourteen minutes. No emulsion formed in this run until the last 2 or 3 cc of "hex" was going into the extractor.

These two runs verified the fact that an emulsion began to form at the time when a small amount of water layer settled to the bottom of the extractor and consequently caused an unfavorable ratio of ether to water layer being pumped. As a result of the observations, it was suggested by Mr. W. C. Rosenbaum that some suitable apparatus should be designed to separate the water layer from the ether-water mixture before the ether layer is returned to the pump. This suggestion led to the next extractor set-up.

E. Extractor Set-up V

A separator was made from a 500 cc Erlenmeyer flask as shown in Illustration IX. The inlet to the separator was connected tangentially to the flask and the outlet was made through a piece of glass tubing inserted through a rubber stopper. This separator was then installed in a set-up as shown in Illustration X. The separator shown in Illustration X is the separator to be used in the next set-up, but the separator made from the 500 cc Erlenmeyer flask was installed in the same place occupied by the separator in Illustration X.

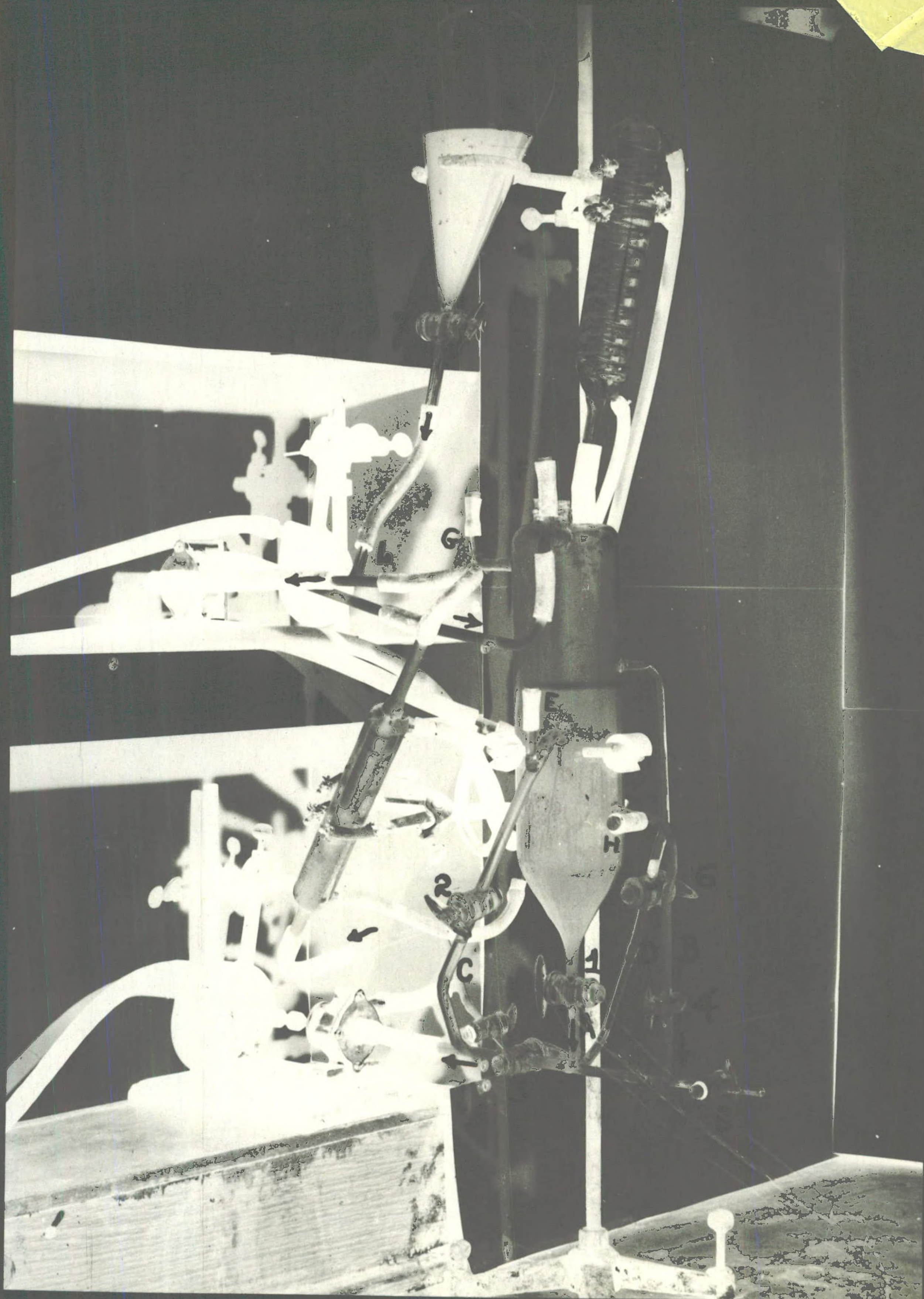


ILLUSTRATION VIII
ADDITION OF "HEX" FROM CHEMICAL S
EXTRACTOR SET-UP IV

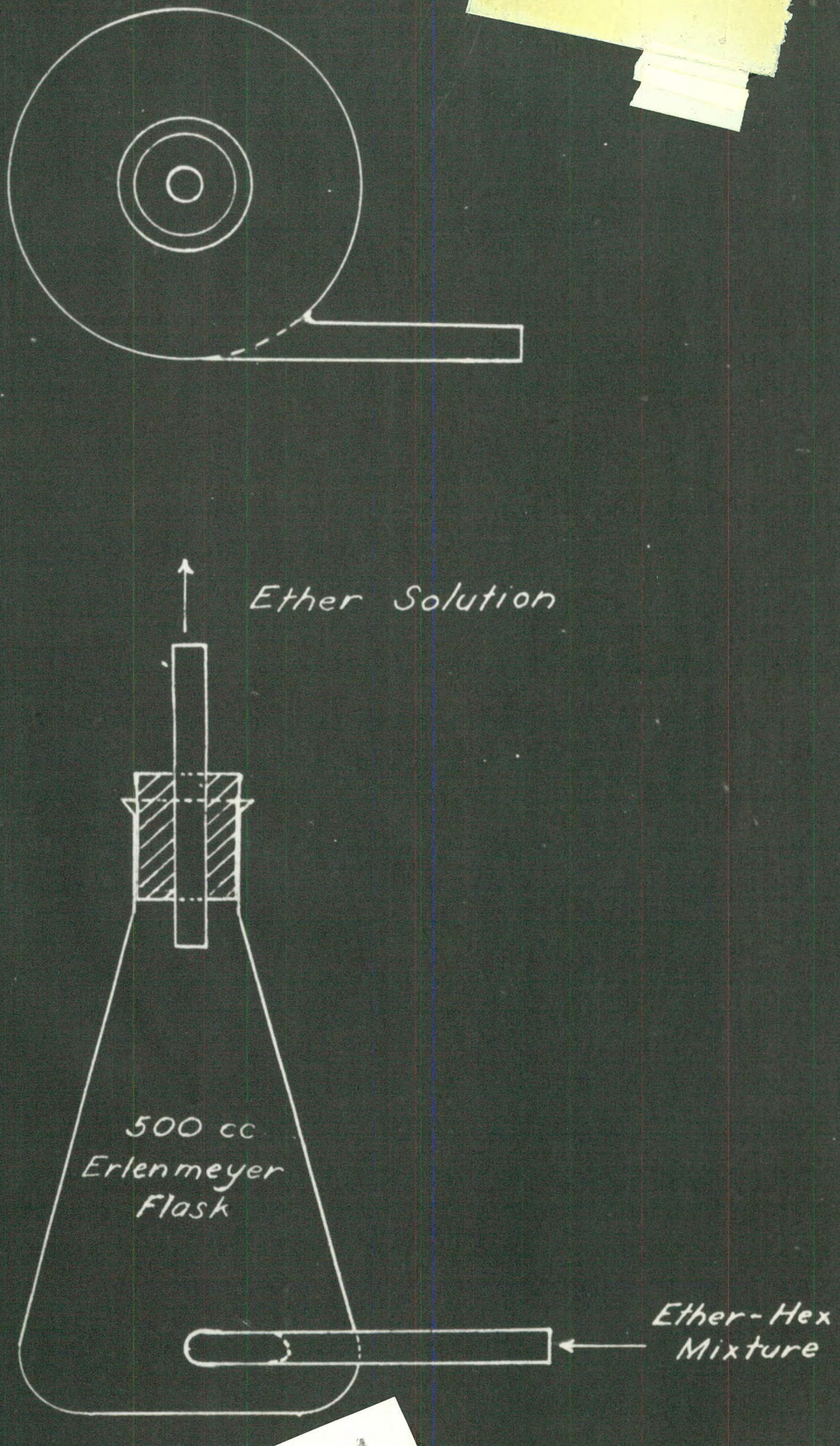


ILLUSTRATION IX
SEPARATOR FOR EXTRACTOR SET-UP V

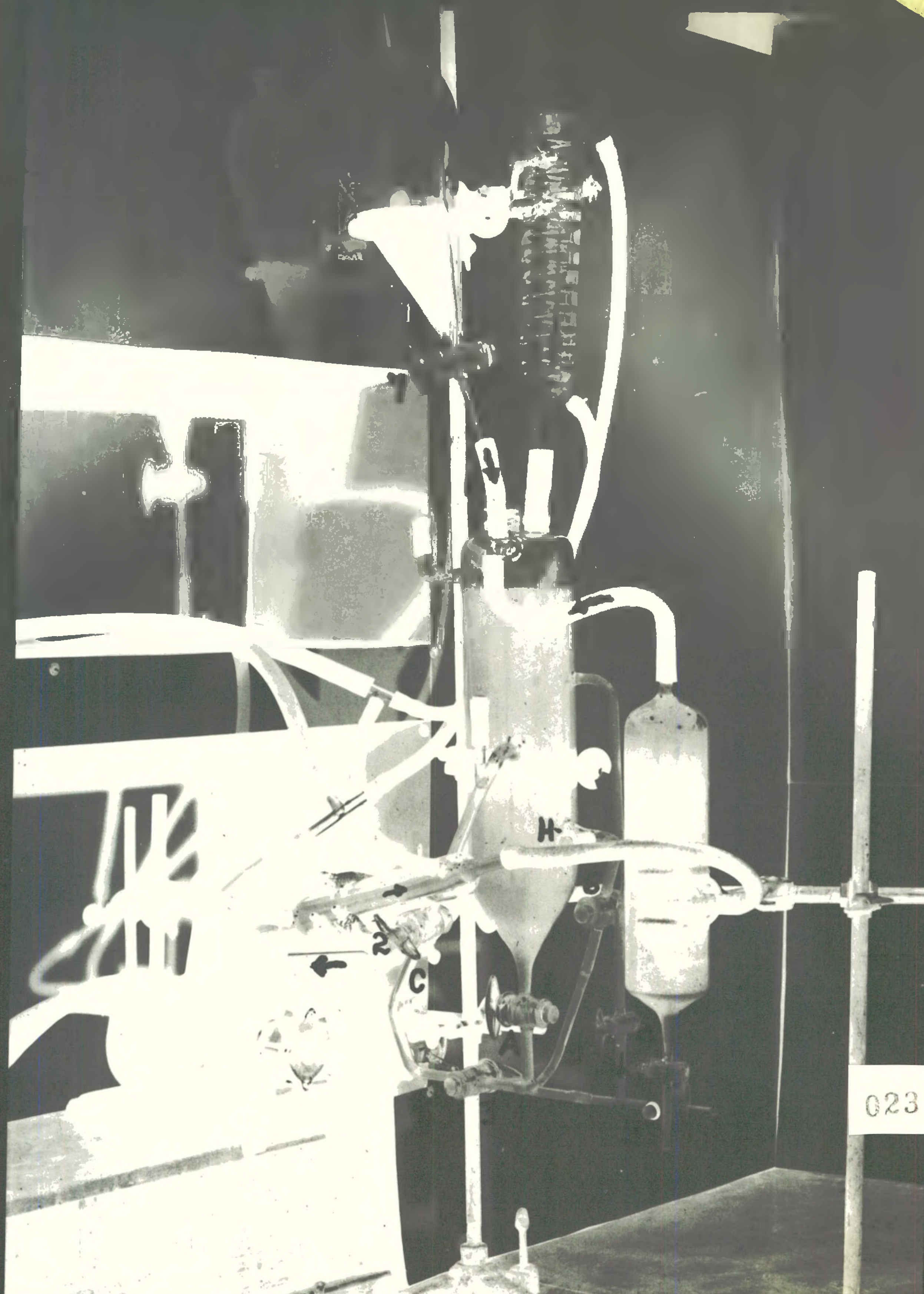


ILLUSTRATION X
ADDITION OF "HEX" FROM CHEMICAL S
EXTRACTOR SET-UP VI

For these runs the "hex" was again added from line F into the return line to the extractor. The ether-"hex" mixture was pumped from the bottom of the extractor through lines A and B through the pump into the bottom of the separator. The water layer settled to the bottom of the separator and the ether layer was returned to the extractor.

Because of the 500 cc separator, the capacity of the extractor was increased from 1500 cc to 2000 cc. Hence, for this set-up 700 cc of "hex" was added to 1200 cc of ether.

Typical data for a run of this set-up is as follows:

Volume of ether at start of run		1200 cc
Volume of "hex" to be added		700 cc
Temperature of ether at start of run		10°C
Temperature of "hex" to be added		70°C
Temperature of mixture after "hex" addition		35°C
Time required to add "hex"		20 min.
Volume of water layer after 4 minutes settling		
(a) In separator	285	
(b) In extractor	160	
Total	445	
Volume of ether layer		1400 cc

In the three runs made with this set-up, no emulsion was formed in any of the runs. After the first run, an attempt was made to form an emulsion by introducing an unfavorable mixture in the pump from the water layer in the bottom of the extractor. An emulsion was formed in the pump and pumped into the separator. However, all of the water layer was pumped from the extractor into the separator before the separator was filled with the emulsion, and as soon as ether solution from the extractor was pumped through the separator, the emulsion in the separator was immediately broken. An emulsion was finally made by by-passing the separator until enough emulsion had formed in the extractor to fill the separator. Then the emulsion was pumped into the separator, leaving some emulsion in the extractor. This emulsion, however, was easily broken by pumping ether layer from line D through the separator.

023 023

This set-up showed very distinct possibilities for two reasons: (1) no emulsion was formed during the "hex" addition and it was difficult to form an emulsion after the "hex" had been added, and (2) the capacity of the extractor can be increased. However, using the separator brings up the question of washing in the plant and this problem will be treated in future experiments.

F. Extractor Set-up VI

Extractor Set-up VI was identical with Extractor Set-up V except that a different type of separator designed by Mr. H. L. Wibbels was used.

This set-up is shown in Illustration X. In this separator the ether-"hex" mixture is introduced tangentially about the middle of the separator. It was hoped that better separation and a more quiescent water layer would be formed in this type of separator. It was also believed that this type of separator would be better for washing the ether layer than the separator used in Set-up V.

One run was made using this type of separator. This run gave results which were identical with the results from the previous set-up. The water layer separated in the separator and no emulsion was formed. This type of separator was no more efficient than the other type, but if this separator idea were to be installed in the plant the cylindrical construction would probably be easier; also, the original plant extractor whose capacity was 100 gallons could easily have been used for one of the separators.

G. Extractor Set-up VII

A new type of separator using a 500 cc Erlenmeyer flask was designed by Dr. J. A. Kyger. This separator is shown in Illustration XI as "hex" is being added to the extractor. This particular separator was designed to try Kyger's idea of washing in which the wash water was added at a slow rate and subsequently separated in the separator. The pumping rate for the ether solution was about 2100 cc per minute and the usual volume of ether solution was about 1500 cc. Hence, if the wash water required per wash is added over a period of three minutes, the ether solution will be circulated four times while the wash water is being added.

023 024

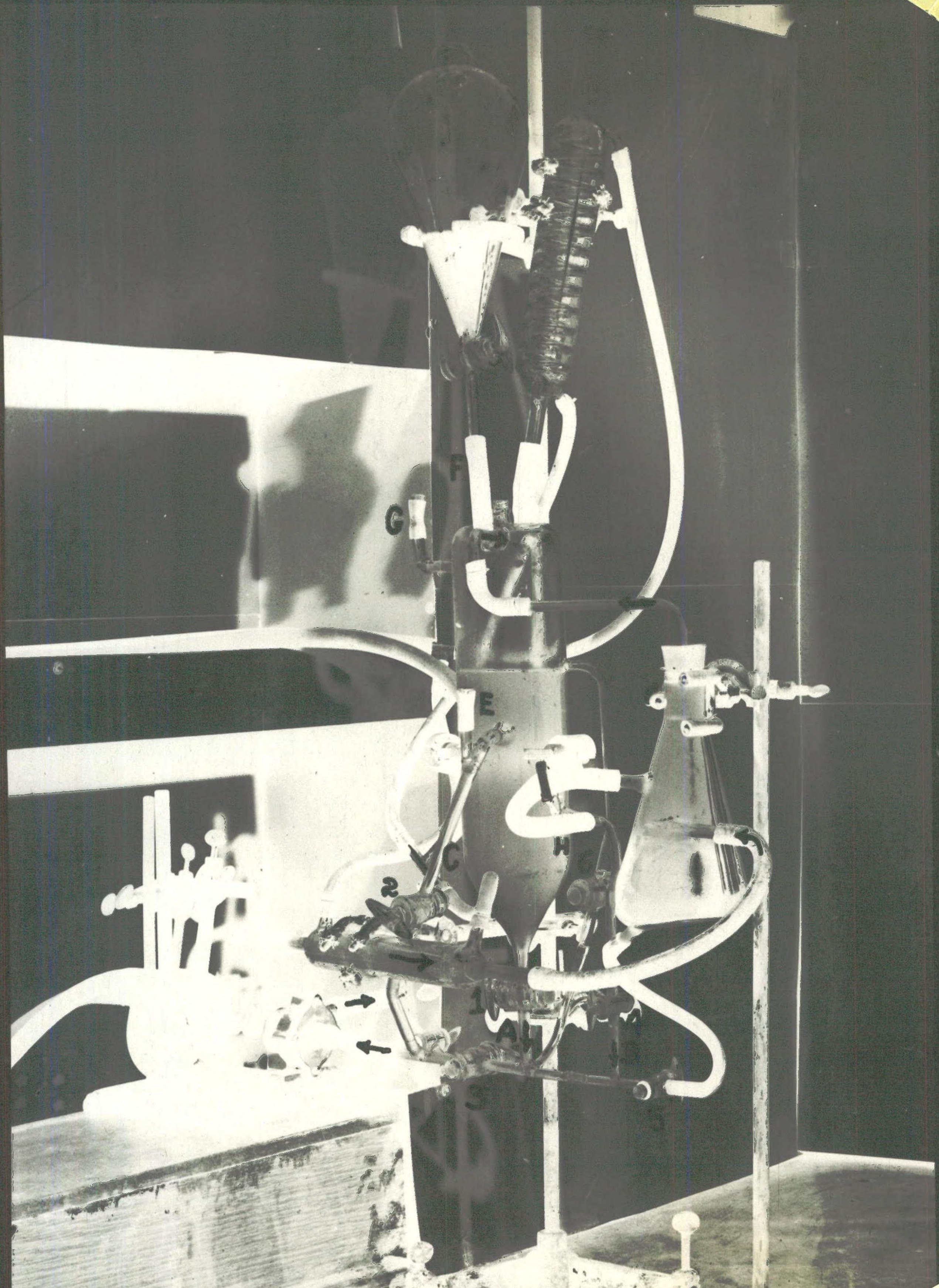


ILLUSTRATION XI
ADDITION OF "HEX" FROM CHEMICAL S
EXTRACTION SET-UP VII

023 025

To try this separator for both "hex" addition and washing, the following experiment was run:

> 700 cc of "hex" was added to 1200 cc of ether as is shown in Illustration XI. Time required for addition of "hex" was about 20 minutes. No emulsion was formed and a water layer of approximately 400 cc was drained after four minutes' settling. Four distilled water washes of 48 cc each were added through the "hex" adding line (f) according to Kyger's method. A sample of the ether layer was tested for Geiger Count after the fourth wash. Data for the washes is shown below.

Wash Number	Wash Water Volume (cc)	Adding Time (minutes)	Geiger Count
1	48	3-1/2	
2	48	3	
3	48	1/2	
4	48	2-1/2	99 min.

Each wash used in this wash procedure was equivalent in volume of water to three washes in the plant extractor. Hence, twelve washes could have been made in the plant extractor with the volume required to wash the ether layer to a Geiger Count of 99 minutes. The ether layer in the plant extractor is usually washed to a Geiger Count of less than 30 minutes after 4 washes.

The separator used in Extractor Set-up VII was as good as the other separators tried. The washing experiment tried by Kyger, however, showed that the separator must either be by-passed in the washing operation or designed in such a manner that the washes will be recirculated through the separator back into the extractor.

H. Extractor Set-up VIII

Because the installation of a separator in the plant would be expensive and also involve a relatively long shut-down period, it was suggested by Dr. H. V. Farr and Dr. C. D. Harrington that some method be devised to eliminate emulsions without drastically changing the plant set-up. Because emulsions were found to be broken when a large amount of ether was mixed with a small amount of water layer, it was suggested by Dr. Farr and Dr. Harrington that the return line from the pump should extend down into the ether layer inside the extractor and thus the return stream would always be mixed with an excess of ether.

The set-up used for this experiment is shown in Illustration XII. The liquor was pumped from the extractor through lines A and B and recirculated into the extractor through the glass tubing which was immersed in the ether layer. The opening on the two pieces of glass tubing were placed opposite each other about 1/4 inch apart. It was hoped that complete mixing would be accomplished between the ether layer and the returning liquor stream by the impinging action of the return stream. The "hex" was added through the side inlet because back pressure of the two impinging streams would not permit addition of the "hex" into the return line.

Only one run was made with this set-up. After the addition of about one fourth of the "hex", an emulsion started forming. As soon as the emulsion began forming, the impinging streams were noticeably slower in velocity and the conditions seemed to be ideal for building up the emulsion.

While this extractor set-up was not successful, the apparatus used was very make-shift. With proper sizing and location of the impinging streams, this extractor set-up might have been satisfactory.

I. Extractor Set-up IX

The separator method for the prevention of emulsions seemed to be the best method at this point, but this method presented problems in installation of proper apparatus and operating problems to obtain proper washing. Extractor Set-up IV seemed to be quite satisfactory for mixing the "hex" and ether in the second pump. Hence, a combination of these two set-ups in which the ether and hex was mixed by a second pump and the water layer was separated in the extractor while the ether solution was being recirculated from a side outlet was suggested.

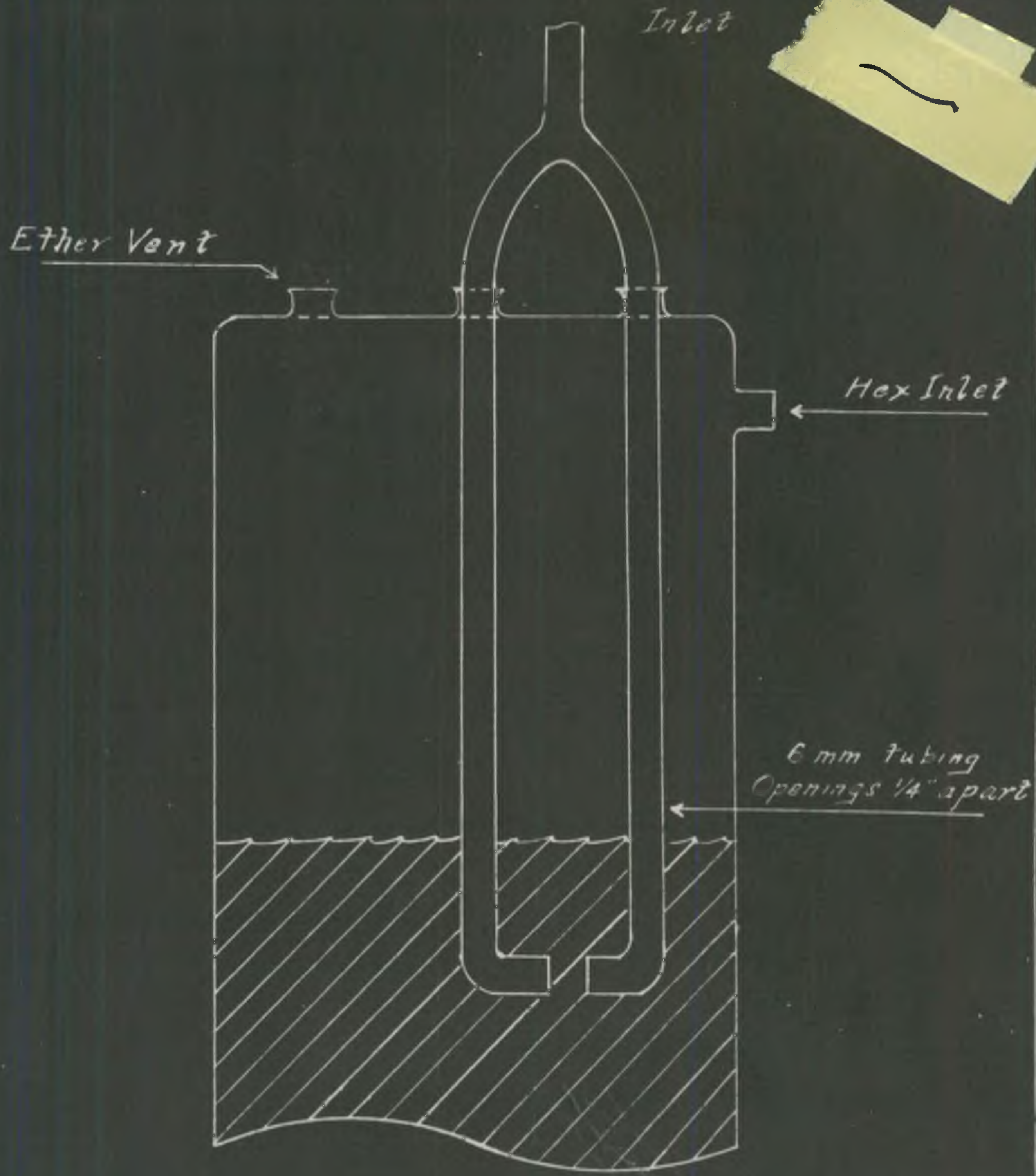


ILLUSTRATION XII
EXTRACTOR SET-UP VIII

023 028

This extractor set-up is shown in Illustration XIII. Line C was added at this time to obtain an outlet in the ether layer at the start of a run. The outlet on line D was not covered with ether layer until about one third of the "hex" was added. In this set-up, ether is pumped from the extractor only through line C and the "hex" is added into the glass T which is located on the inlet side of the second pump.

1) Extractor Set-up IX, Run 1

The first run in this set-up was made with stop-cocks 1, 4, 5, and 6 closed and stop-cock 2 open. Stop-cock 3 was not on the extractor at this time.

Data from Run 1

Volume of ether at start of run	900 cc
Volume of "hex" to be added	500 cc
Time required for "hex" addition	14 min.
Volume of ether layer at end of run	1065 cc
"Hex" content of ether layer	866 grams
Volume of water layer at end of run	215 cc
"Hex" content of water layer	115 grams
Extraction efficiency	88.3%

No emulsion was formed during the run and no other trouble was encountered.

2) Extractor Set-up IX, Run 2

The first run with this set-up gave very good results in both operating conditions and extraction efficiency; however, it was decided to make a check run in which the water layer would be recirculated until equilibrium conditions were reached. The same hex which was used in the previous experiment was used in this run.

The "hex" was added at the same point as in the previous run, but stop-cocks 1 and 4 were open to allow the water layer to recirculate. An emulsion was formed near the end of the "hex" adding period, but this emulsion was easily broken by the method described in Extractor Set-up I.

023 029

ILLUSTRATION XIII
ADDITION OF "HEX" FROM CHEMICAL S
EXTRACTOR SET-UP IX

Data from Run 2

Volume of ether at start of run	900 cc
Volume of "hex" to be added	500 cc
Time required for "hex" addition	16 min.
Volume of ether at end of run	1100 cc
"Hex" content of ether layer	874 grams
Volume of water layer at end of run	215 cc
"Hex" content of water layer	147 grams
Extraction Efficiency	85.3%

It is apparent by comparing the extraction efficiency of both runs that better extraction is being attained when the water layer is not recirculated. This is probably due to the fact that the first portion of "hex" is extracted more efficiently from the "hex"-free ether than the last portion of "hex" is extracted from the concentrated "hex"-ether solution. Hence, the water layer from the initial extraction would extract "hex" from the ether layer if this water layer were recirculated.

3) Extractor Set-up IX, Run 3

With the set-up used in Run 1, the water layer was separated as the "hex" was being added. However, the water layer was not drained until all of the "hex" had been added. It was then discovered that if a stop-cock would be installed between lines A and C, the water layer could be drained while the "hex" was added by closing this stop-cock (3) and draining from stop-cocks 1 and 4 through stop-cock 5. Hence, stop-cock 3 was added to the extractor and this extractor set-up is shown in its exact form in Illustration XIII. This illustration shows the "hex" being added through line L, while ether is recirculating through line C and the water layer is being drained through stop-cock 5. In runs 1 and 2 with Extractor Set-up IX, 500 cc of "hex" was added to the extractor. With this set-up, however, 650 cc of "hex" was added--an increase of 30% in the capacity of the extractor.

A number of runs were made with this set-up, using alltypes of plant liquor, and all runs were made with no emulsion trouble. The typical data for the runs would be similar to the data for Extractor Set-up IX, Run 1, with the exception that 650 cc of "hex" was added to 1100 cc of ether.

Washing the ether layer in this set-up was no problem because the regular plant wash procedure could be used if stop-cocks 2 and 3 were open while the wash was being recycled.

The plant procedure for the water extraction of the O.K. liquor in the plant extractor was to add distilled water equal in volume to about one third the volume of the ether layer, recycled the mixture for two minutes, settle for four minutes, and drain the water layer into the O.K. liquor tank. It is obvious that with the set-up of continuous drainage of the water-layer while "hex" is added, the extractor may be filled almost to the top, leaving no room for distilled water to be added for the extraction of the O.K. liquor. However, since the "hex" was extracted by ether by adding the "hex" in the return ether line, it seemed reasonable to believe that the "hex"-ether solution could be extracted by adding the distilled water in a manner similar to the addition of "hex". Hence, line E was added to the extractor and a connection was made from this line to a funnel which contained distilled water.

To make a distilled water extraction with this set-up, the ether solution was recirculated through line C with stop-cock 3 closed, and distilled water was slowly added through line E. As soon as a water layer began to form, this layer was drained through stop-cock 5 at a rate equivalent to the addition of water. The water extraction method is shown in Illustration XIV. The ether layer has been dyed with Du Pont Anthraquinone Green G Base so that the two layers may be distinguished.

For an average run in the plant, 300 gallons of distilled water must be added to extract 300 gallons of ether solution. The average run with the new laboratory set-up required 1100 cc of water to extract 1500 cc of ether solution. Hence, about 25% less water is required to extract by the continuous addition of water with continuous draining.

This set-up would result in both a saving in water and steam and also a saving in time required for extraction of good liquor and the concentration of good liquor.

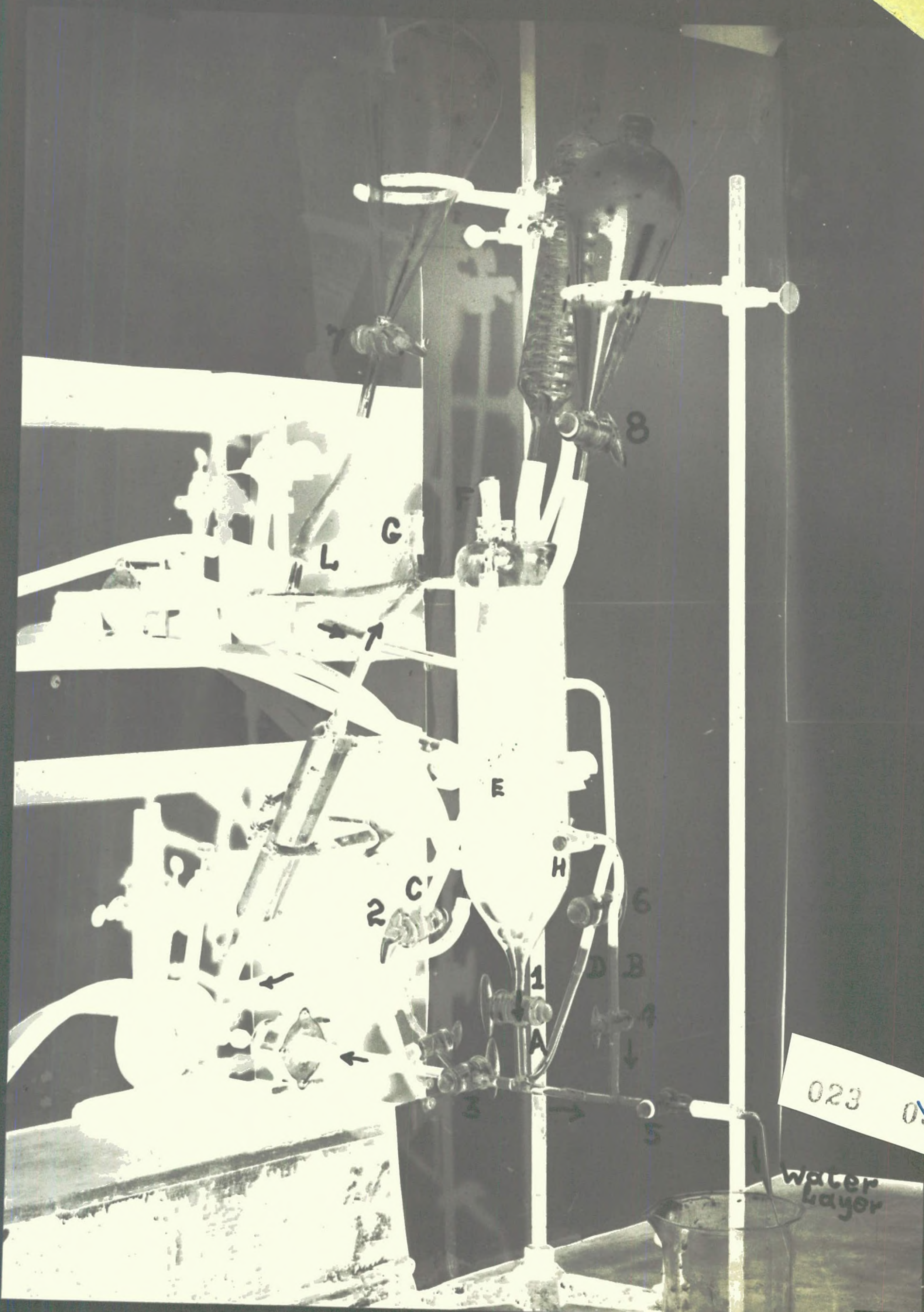


ILLUSTRATION XIV
WATER EXTRACTION OF WASHED ETHER SOLUTION
EXTRACTOR SET-UP IX

VI. Recommendation for Changes in Plant Extractor

As a result of the experimental work done on the prevention of emulsion, it was recommended that the plant extractors be altered to a set-up which corresponds to Extractor Set-up IX, the advantage to this set-up being as follows:

1. No emulsion should be formed with types of material being used in the plant.

2. The efficiency of the ether extraction will be slightly increased.

3. No washing problem should occur after the alterations, because the washing procedure will be essentially unchanged.

4. The volume capacity of each extractor will be increased by approximately 30%.

5. The time required for water extraction will be reduced.

6. The amount of water required for the water extraction will be reduced.

7. The alterations are relatively simple and should not be expensive or lengthy.

VII. Plant Changes to Prevent Emulsions

A. Engineering Details of Extractor Alterations

Plans were drawn by Mr. W. C. Rosenbaum and the necessary pipe fittings were ordered. In addition to the pipe fittings, two 5 HP motors, two 1-1/2" CG Worthington Pumps, and one new "hex" measuring tank (260 gallons) for the South extractor were ordered. The "hex" measuring tank on the South Extractor was to be used to replace the one on the North Extractor.

The plans as drawn are shown on the schematic piping diagram. In order to make room for Section A, it was necessary to move the pump on each extractor back about eighteen inches. The job of moving the pump back could not be started until the plant was shut down, but all of the piping shown in Section A could be cut and fitted to be inserted in place as soon as the pump could be moved back. Section A was to be connected to the side of the extractor through a full coupling to be welded on the side of the extractor. The purpose of the coupling was to provide means of connecting piping inside the extractor in case the height of the side outlet needs to be changed.

The pumps which were to be installed near the top of the extractors could be installed before the extractors were shut down. Also the piping in Section B could be cut and fitted to be inserted as soon as the shutdown was made.

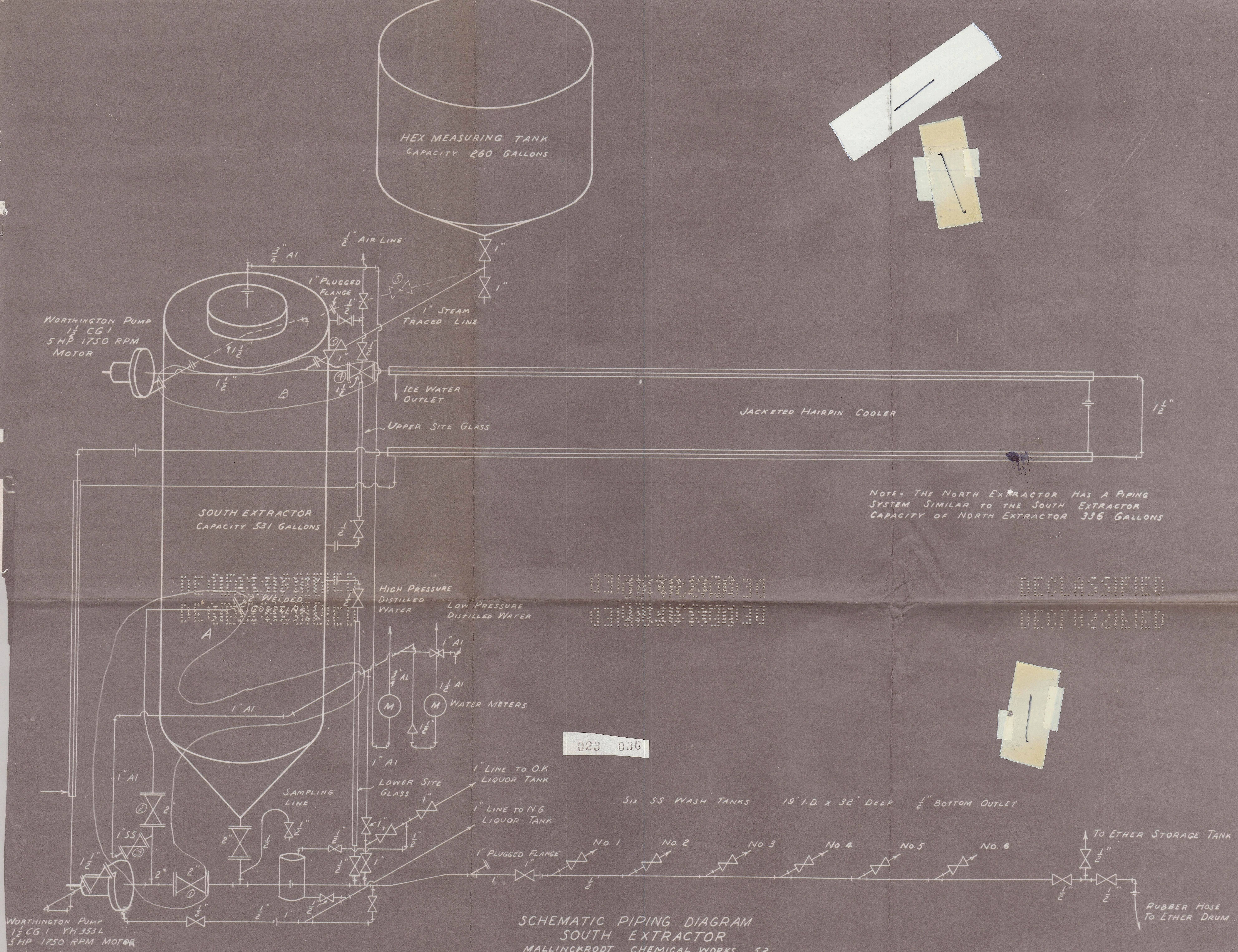
Because it was possible that both extractors might be draining simultaneously into either the O.K. liquor tank or the N.G. liquor tank, plans were made to change the drain lines to these two tanks so that either extractor could drain independently into either tank.

A number of other small details, such as planning for reinforcing the stand for the new "hex" measuring tank, planning for running distilled water piping to the water seals on the pumps, planning to alter the cooling water piping systems when the cooling hairpin was moved back, and several other smaller items were foreseen and much preliminary work was done to decrease the shut-down time required to make the changes.

B. Alteration of the Extractors

Work was begun on the extractors at 8:00 A.M., November 11, 1944, and the work was completed at about 6:00 P.M. the following day. The total working time was eighteen hours and the total shutdown time was forty-two hours.

All of the work was completed as shown on the schematic piping diagram, the only exception being that the "hex" adding lines were not steam traced.



SCHEMATIC PIPING DIAGRAM
SOUTH EXTRACTOR
MALLINCKRODT CHEMICAL WORKS 52
DRAWN - 3/18/45 BY - H. YEAGER

C. First Runs on Extractors after Alterations

As soon as the alterations were completed, both extractors were filled to the desired height with ether, and "hex" was added to the extractors according to the new method. Valve 1 was closed. Valve 2 was opened, and the ether was re-cycled from the side outlet through both pumps. (Both pumps were wired to operate simultaneously from one switch; though, if desired, the original pump could be operated when the new pump on the second floor was not running.) "Hex" was added through Valve 5 into the return ether line.

The first run was made in the North Extractor (Run 269) using "hex" from sodium salt. "Hex" addition was begun at 9:20 P.M., and the addition of "hex" proceeded satisfactorily until about one fourth of the "hex" had been added. During this time no emulsion had formed and the water layer was easily drained into the N.G. tank. However, after one fourth of the "hex" had been added, the "hex" would not enter the return line unless valve 4 was almost completely closed. With valve 4 almost completely closed, an emulsion began to form because of the deficiency of ether in the second pump. It became necessary to add the "hex" in portions of about 20 gallons. After each small addition of "hex", it was necessary to re-cycle with valve 1 open in order to break the emulsion which had formed. All of the hex was finally added by this method and the water layer was completely drained at 11:10 P.M., re-quiring a "hex" addition time of one hour and fifty minutes. The specific gravity of the ether solution at this time was 1.27.

The regular plant washing procedure was then followed with two exceptions: (1) the volume of wash water for each wash was three gallons instead of 2-1/2, and (2) Valves 1 and 2 were left open while each wash was recycled. The water layers after each wash appeared to be dirtier than usual, and the ether layer was washed twelve times to insure O.K. goods. However, it was believed that the dirty washes were caused by the materials left in the extractor while the charges were being made, and subsequent runs proved that the washing procedure was not affected by the extractor changes.

The water extraction of the ether solution was easily accomplished by the new method. Distilled water was added through Valve 3 at a rate of about seven gallons per minute while the ether solution was being pumped through the side outlet, Valve 1 being closed. The water solution which settled was then drained into the O.K. liquor tank while the extraction water was being added. 200 gallons of water was used to extract the ether solution and 35 minutes was required to complete the water extraction.

The second run by the new method was tried on the South Extractor (Run 270) using the same "hex" as in the previous run. The results of this run were similar to the results of Run 269 on the North Extractor. The "hex" addition was difficult by the new method, but the washing procedure and water extraction procedure were both satisfactory.

Because of the difficulty encountered in adding "hex" by the new method, the "hex" adding line was temporarily changed to enter the "hex" through the old "hex" inlet on the side of the extractor until necessary changes could be made to introduce the "hex" at the proper place.

On the next run in the North Extractor with "hex" being added by the old method with continuous drainage of the water layer by the new method, the time required for "hex" addition was fourteen minutes and the specific gravity of the ether layer was 1.330. On the next run in the South Extractor under similar conditions, the time required for "hex" addition was twenty minutes, and the specific gravity of the ether layer was 1.410. In both runs, no emulsion was formed. Hence, from the specific gravities obtained and the fact that no emulsion formed in these two runs, it appeared that the only reason for adding the "hex" into the return ether stream would be to possibly increase the efficiency of the ether extraction.

D. Further Changes in the Extractor System

It was believed that two factors were responsible for the difficulty encountered in the addition of "hex" into the return ether line: (1) pressure surges in the line caused by boiling ether when the "hex" and ether is mixed, and (2) hydraulic pressure building up at the point where "hex" was being added. It is quite likely that both of these factors were causing trouble.

A mercury manometer was attached to the opening used to add "hex" into the return line, and readings were taken of the pressure at this point while "hex" was being added into the old "hex" inlet. The pressure at this point increased from a slightly negative pressure at the beginning of the run to a positive pressure of seven inches of mercury at the end of the run. Hence, the pressure would be acting against the addition of "hex" during the latter part of the "hex" addition when the static pressure of the "hex" was least.

It was obvious that the "hex" could not be introduced into the return ether line unless some means were provided to put the "hex" under pressure. This could be accomplished by raising the "hex" measuring tanks, by sealing the tanks and putting them under air pressure, or by pumping the "hex" into the return ether line. In view of the good extractions being obtained by adding the "hex" into the old inlet, it was decided to quit working on a method for adding the "hex" into the return ether line.

The return line emptied inside the extractor vertically downward through a 90° elbow which was located about six inches from the side of the extractor where the "hex" enters. When "hex" was added, only a small portion of the recycling ether contacted the "hex" being added. Hence, the 90° elbow was replaced with a 45° elbow and the pipe was positioned so that the returning stream hit about one half inch above the "hex" inlet. This position was chosen after watching the actual mixing of the "hex" and ether streams with the return pipe in various positions.

Data was taken to determine the efficiency of the ether extraction and the efficiency was found to be satisfactory. (See VI-E: Efficiency of Ether Extraction.) Hence, the "hex" adding line was permanently installed in its old position and Section B was replaced with a single piece of 1-1/2-inch pipe.

E. Efficiency of Ether Extraction

In the old method of extraction, the "hex" and ether were continuously recycled and, although the "hex" and ether were probably never completely mixed, it may be assumed that the efficiency of ether extraction would be no better than the efficiency obtained at equilibrium conditions. It was desired to compare the efficiency of the extractors under the new set-up with the efficiency of the extractors in the old set-up. Hence, the efficiency of the plant extractors was obtained by measurements and assays of the "hex" added and the ether solution obtained. This efficiency was compared with the shake-out efficiency obtained when the same "hex" was added to an equivalent amount of ether in a laboratory extractor. For these efficiencies, the funnel-shaped extractor with the air-driven glass stirrer was used.

Extractor	Type of Liquor Added	Lbs. X Added to the Extractor	Lbs. X Extracted	Efficiency of Plant Extraction %	Efficiency of Shake-out Extraction %
North	162	1270	1050	82.6	80.7
South	162	1935	1605	82.9	80.7
North	S2	631	492	78.0	86.2
South	S2	896	716	79.9	86.2
North	162	1198	962	80.3	76.3
South	162	1970	1675	84.8	76.3
South	162	1874	1585	84.6	80.7
North	162	1258	1001	[illegible]	80.7
South	S2	1018	794	78.0	79.4
South	S	1542	1357	87.8	79.4

The accuracy of these efficiency calculations was probably ±3% because of the inaccuracy of measurements, samples, and assays. However, the results do indicate that the efficiency of extraction under the new set-up is probably as good as if not better than the extraction efficiency was under the old set-up. The only material which apparently gave poorer extraction efficiencies was S2.

F. Emulsions in New Set-up

Since the time the extractors were changed to March 24, 1945, 1263 runs have been made in the extractors. During this time only one emulsion has been formed in the plant extractors, and this emulsion could not be explained because the material which was used in the run which made the emulsion did not cause any emulsion in subsequent runs.

Also, under the new set-up, the N.G. liquor from sodium salt which has gone through the extractors once may be sent back to the extractors without any preliminary chemical treatment. Recovery cake, which had heretofore been dissolved and re-precipitated, could now be dissolved and sent to the extractors without preliminary chemical treatment.

G. Increase in Productive Capacity

The productive capacities of the extractors were increased considerably by the alterations in the extractors. In the first place, the working volume of each extractor was increased by the continuous draining method. 145 gallons of "hex" may now be added to the North Extractor instead of 115 gallons, and 217 gallons of "hex" may be added to the South Extractor instead of 165 gallons. This represents a 34% increase in the volume capacity of the two extractors.

Also, the productive capacity of the extractors has been increased because of a decrease in the time required for a complete extraction run. During 100 runs in both extractors previous to the time the extractors were altered, the average time required for a complete run was three hours and fifty-two minutes. For 100 runs in both extractors after the changes had been made, the average time required for a complete run was three hours and fifteen minutes. Thus an increase of 16% in the productive capacities of the extractors was realized because of the shortened time cycle.

H. Purification of Ether Solution

Since the time the extractors have been changed, no finished lots have received a shotgun analysis greater than 0.05%. Hence, it is apparent that the new extractor system has the same washing qualities as the old extractor system.

HYeager
map

023 041