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A STUDY OF ETHER EXTRACTION OF URANYL NITRATE HEXAHYDRATE LIQUORS WITH SPECIAL REFERENCE TO THE FORMATION OF EMULSIONS

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A STUDY OF ETHER EXTRACTION
OF URANYL NITRATE HEXAHYDRATE LIQUORS
WITH SPECIAL REFERENCE TO THE FORMATION OF EMULSIONS

I. PURPOSE MCW-4

To discover the cause of emulsions in the ether extraction of uranyl nitrate hexahydrate and to possible design changes in plant extractors to prevent emulsions.

II. DISCUSSION

When molten uranyl nitrate hexahydrate $[UO_2(NO_3)_2 \cdot 6H_2O]$ is added to ether in a batch extractor and mixing is obtained by a centrifugal pump, a slow settling emulsion is a frequent occurrence. In this report an emulsion will be defined as a mixture of ether and water solutions of uranyl nitrate which has been formed in such a manner that two phases will not quickly separate.

When emulsions are formed in the plant extractors, considerable loss in the production of UO_2 occurred. This loss in production occurred for two reasons: (1) a longer period of time was required for separating the liquids in the extractor; and (2) the efficiency of extraction was lowered because of excessive drainage of ether extract along with the water layer.

The only methods used to prevent emulsions had been chemical methods which were found to help in particular types of material;

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however, no chemical treatment was known which would eliminate the problem.

Because the production loss from emulsions was a very serious problem, a series of experiments was performed to obtain a test which could predict an emulsion in the plant extractors and also to obtain a better picture of the formation of emulsions.

III. EXPERIMENTAL WORK

A. Preliminary Experiments

In the period from the latter part of 1942 to the latter part of 1943, all material which was suspected of being capable of emulsion formation was tested by an extraction test to see if an emulsion was formed. This extraction test was performed by adding 100 ml of molten impure $UO_2(NO_3)_2 \cdot 6H_2O$ to 170 ml of chilled ether in an open conical glass extractor in which the contents were mixed by a glass stirring rod which was powered by an air motor. However, this test was inadequate because material which gave a good extraction test might easily form an emulsion in the plant extractors 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 methods of mixing in the extraction test and the plant extractions were not similar.

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In order to obtain a laboratory extractor similar to the plant extractor, a 1500-cc glass extractor was made. This extractor in its final form after a number of changes is shown in Figure 1. The original extractor may be visualized by eliminating lines D, C, H, and F and stop-cock 3. The liquor is recycled by a small Eastern Pump which is powered by an air motor. The liquid is cooled by recirculation through a single-pass glass heat exchanger and ether is condensed and re-fluxed into the extractor by the spiral condenser. Molten uranyl hexahydrate is added from a separatory funnel through line G.

An attempt was made to use this extractor for the control extraction test. However, this apparatus was not satisfactory for a control test; in general the control extractions in this apparatus made more emulsions than the plant extractors.

Although the model extractor was rather unsuccessful as a control test apparatus, a number of runs was made to study the actual conditions which existed in the formation of emulsions with a centrifugal pump. It was during two of these random experiments that observations were made which led to other experiments which were successful in the prevention of emulsions.

During one random run, a very thick emulsion was formed which filled about two-thirds of the extractor. This emulsion was recycled for about ten minutes, but the amount of emulsion

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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 solution 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 settled. Instead of filling the extractor full of emulsion by this method, the emulsion was entirely broken and a complete separation of the two phases was attained.

During another run an attempt was made to study the removal of an emulsion by successively draining small water layers and recycling and settling the remaining emulsion until all the emulsion has been separated into two phases. After the emulsion had been recycled, settled, and water layer drained two times, the emulsion had been reduced to the point where the emulsion layer was not as high as the inlet to the sight-glass (Line B). When the pump was started again for recycling the emulsion, the pump began pumping a large amount of ether solution 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 of the extractor and

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dispersed into the ether layer until all of the emulsion had disappeared. When the pump was stopped, a complete separation of the two phases was attained in less than two minutes.

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 emulsion layer in the bottom of the extractor.

B. Extractor Set-up I

The extractor set-up for the first experiment may be visualized from Figure 1 by eliminating lines C, H, F, and stop-cock 3.

A typical run with this set-up is shown in Figures 2, 3, 4, and 5. In these photographs, however, line C is used 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.

In this run the molten liquor is added to recycling ether which is being pumped only from the bottom of the extractor. Figure 2 shows the condition in the extractor after about two-thirds of the molten liquor has been added. Molten liquor is being added through line G while the mixture is being recircu-

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lated from line A and B through the heat exchanger into the top of the extractor.

As the mixture 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 solution, whereas the lower two-thirds of the extractor contains the emulsion which is being recirculated. The liquid recirculating is a heavy, viscous liquid which immediately falls through the ether layer.

Figure 3 shows the condition in the extractor after all the molten liquor has been added and the mixture has been allowed to settle for four minutes. At this time, the separated water layer, which can be seen in the sight-glass, was rising very slowly. In ordinary plant practice, this separated water layer would be drained and the remaining contents of the extractor would be recirculated again.

The emulsion was then broken in the following manner. 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 was filled with ether extract instead of emulsion, stop-cock 1 was opened about half way and stop-cock 4 was completely opened. Figure 4 shows the mixture circulating as the emulsion is being broken. By inspecting Figure 4, the reader will notice

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that lines C and B have a light-colored liquid in them, whereas line A contains the dark emulsion; also, there is a mixture of ether and water solutions in the top of the extractor, which did not occur in Figure 2. Under these conditions, the emulsion layer will gradually drop and be dispersed into the ether layer in the top of the extractor. As soon as the mixture going through line A is the same as the mixture going through lines B and C, the emulsion will be broken.

Figure 5 shows the complete separation attained in a two-minute settling period after the emulsion was broken. Comparison of Figure 5 with Figure 3 will show the reader the amount of ether extract which would have been lost if the emulsion could not have been broken.

Typical data for a run would be as follows:

Volume of ether at start of run	850 ml
Volume of liquor to be added	500 ml
Temperature of ether at start of run	10°C
Temperature of liquor to be added	70°C
Temperature of mixture after adding liquor	35°C
Time required for addition	15
Volume of water separated after four minutes' settling	150 ml

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Volume of emulsion after four minutes' settling	550 ml
Volume of ether layer after four minutes' settling	550 ml
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

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

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C. Extractor Set-Ups II and III

Because there was some doubt as to the ability of Set-up I to be workable in the plant extractors, 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 that the molten liquor could be mixed with the ether before it entered the extractor by introducing it into the return line from the pump. It was thought that the water solution would be dispersed into the ether layer and not allow an unfavorable ratio of water solution to ether solution entering the pump. Extractor Set-up III was used to see if emulsion formation could be prevented by this method.

This extractor set-up is shown in Figure 6 in which molten liquor is being added through line F. For this set-up, lines C, D, H, E, and G were not used. In this photograph, no emulsion had begun to form, whereas, if the liquor had been added through line G instead of F, an emulsion would have started to

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form. Using this set-up, however, an emulsion usually started forming about the time one half of the molten liquor had been added.

One of the reasons for Extractor Set-up II not working was believed to be insufficient mixing of the two phases in the line entering the extractor. In order to obtain better mixing, a pump was inserted in the return line to the extractor beyond line L where the molten liquor is added. Extractor Set-up III as shown in Figure 7 shows this arrangement while molten liquor is being added.

Two runs were made with this set-up. In both runs no emulsion formed until nearly all the material had been added; however, an emulsion did form during the latter part of the run.

D. Extractor Set-up IV

Because the experiments in which an attempt to prevent an emulsion with complete mixing of the two phases were unsuccessful, it was decided to attempt an extraction in which the major portion of the water phase is separated in an auxiliary decanter.

Extractor Set-up IV for this experiment is shown in Figure 8. Molten liquor is being added through line F and the ether phase plus a small portion of the water phase is

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being recirculated with the pump through the decanter where most of the water phase is separated and the remaining ether and water phases are returned to the extractor. The dark-colored liquor in the decanter is the separate water layer and the light-colored liquor in the top of the decanter and in the extractor is the ether solution with a small amount of water solution. Three runs were performed with this set-up and in each run no emulsion was formed.

This set-up was advantageous for two reasons: (1) no emulsion could be formed, and (2) the capacity of the extractor could be increased by the volume of the decanter. However, there was some doubt that the ether solution could be easily purified by water washes if the wash water were to be separated in the decanter in this set-up.

E. Extractor Set-up V

The decanter method for the prevention of emulsions was very successful, but this method presented problems in installation of proper apparatus and operation problems to obtain proper washing. The mixing of recycling ether and molten liquor in a secondary pump had proved to be a satisfactory mixer. Hence, a combination of these two methods was suggested in which the ether solution be recycled from a side outlet on the extractor and molten liquor be added to the inlet side of a secondary pump in the recirculating line. In this set-up the pump is the

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mixer and the extractor is the decanter. In the first few experiments, the water phase was allowed to separate completely in the extractor before separating the phases. In later experiments, however, the water phase was drained continuously while the molten liquor was being added.

A run using Set-up V is shown in Figure 10. Ether is being recirculated from line C by both pumps. Molten liquor is being added through line L. The ether and water phases are separated in the extractor with the ether phase recycling and the water layer being drained continuously.

This extractor set-up was very successful in the prevention of emulsions and was found to have a better extraction efficiency than the extraction method where both phases are completely mixed. The ether extraction efficiency in one run by this method was 88.5%, but when both phases from this run were completely mixed, the ether extraction efficiency was only 85.3%. Also, by continuous drainage of the water phase, it is possible to utilize more of the capacity of the extractor to contain ether phase instead of the water phase.

This set-up was found to be the most promising and it was decided to alter the plant extractors to be similar to this set-up.

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IV. SUMMARY

A laboratory extractor similar to plant batch extractors was constructed and experiments were run to study the characteristics of emulsion formation of a mixture of ether and impure uranyl nitrate hexahydrate being mixed by a centrifugal pump. Experiments were performed which show that the fundamental factor in the formation of emulsions of this type was the ratio of water phase to ether phase being mixed in the pump. High ratios will cause emulsion and low ratios will prevent or break emulsions.

A number of changes were made in the laboratory extractor which utilized this factor to advantage in preventing emulsions. The most promising change from the standpoint of emulsion prevention, ease of alteration, and productive capacity was a set-up in which the ether and water phases are separated in the extractor while ether is being recirculated from a side outlet in the extractor through two pumps with impure molten uranyl nitrate being added to the inlet side of the second pump.

The plant extractors were altered to be similar to this set-up and no further trouble was encountered with emulsions in the plant extractors.

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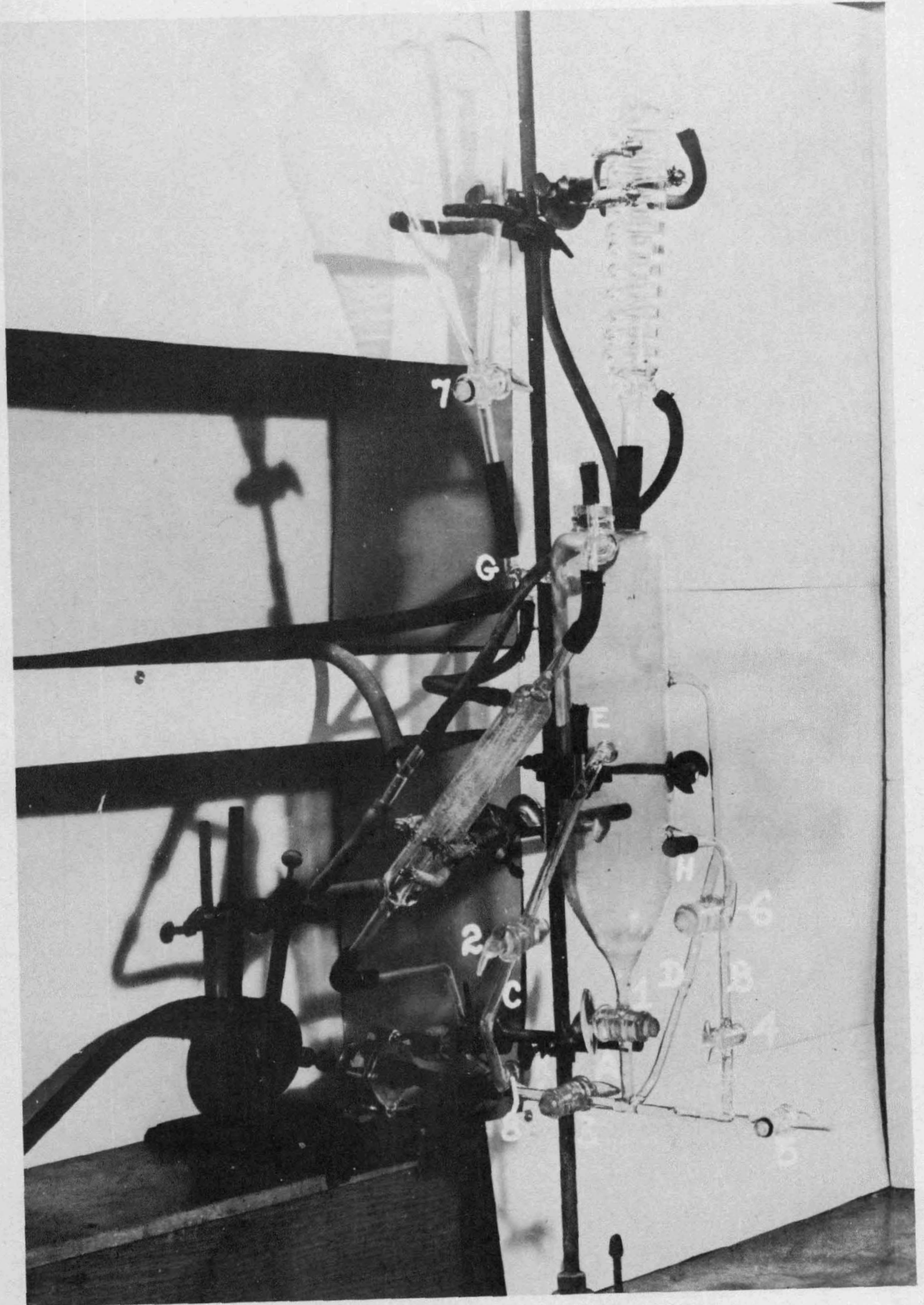


Fig. 1--Model extractor.

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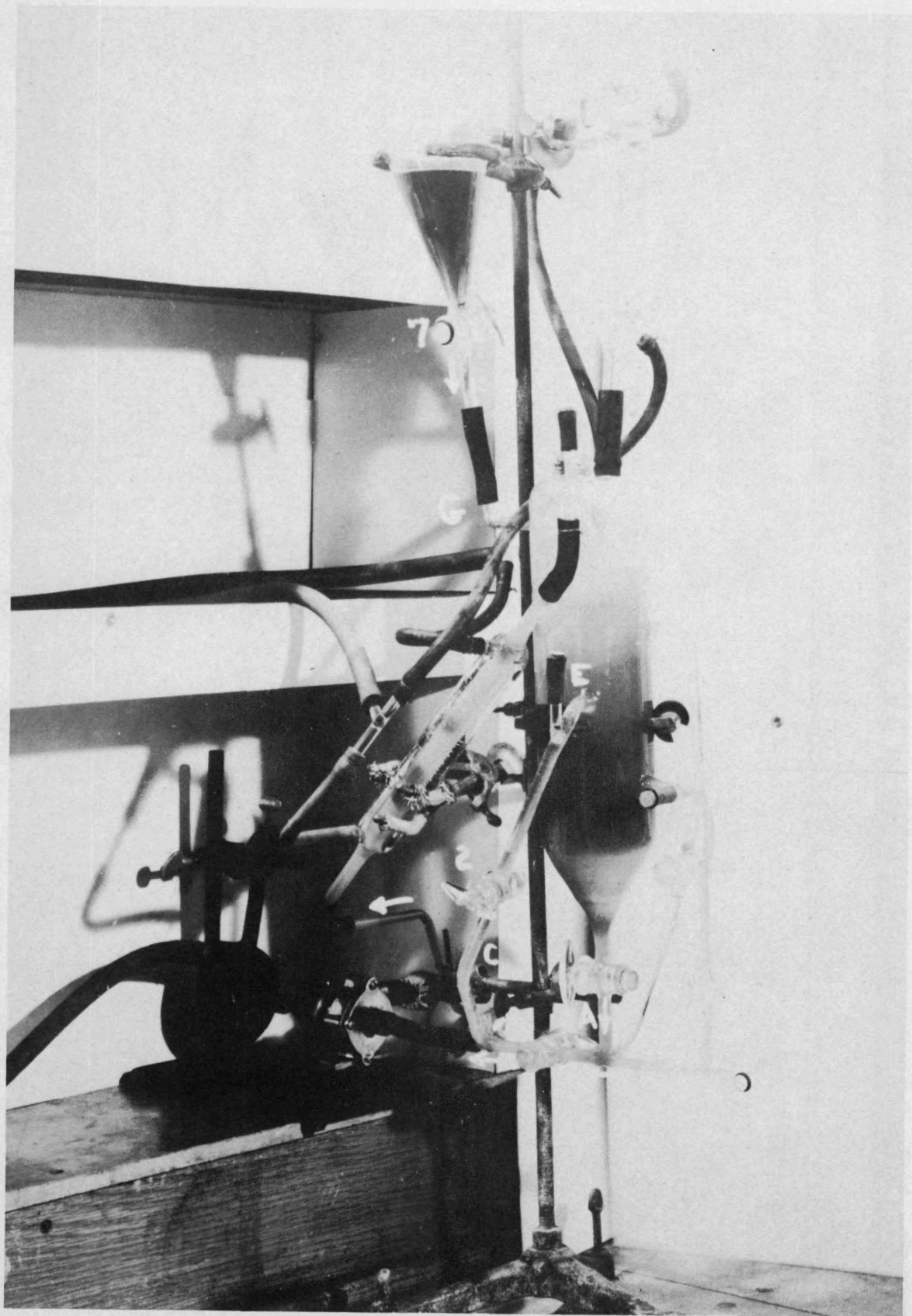


Fig. 2--Formation of an emulsion.

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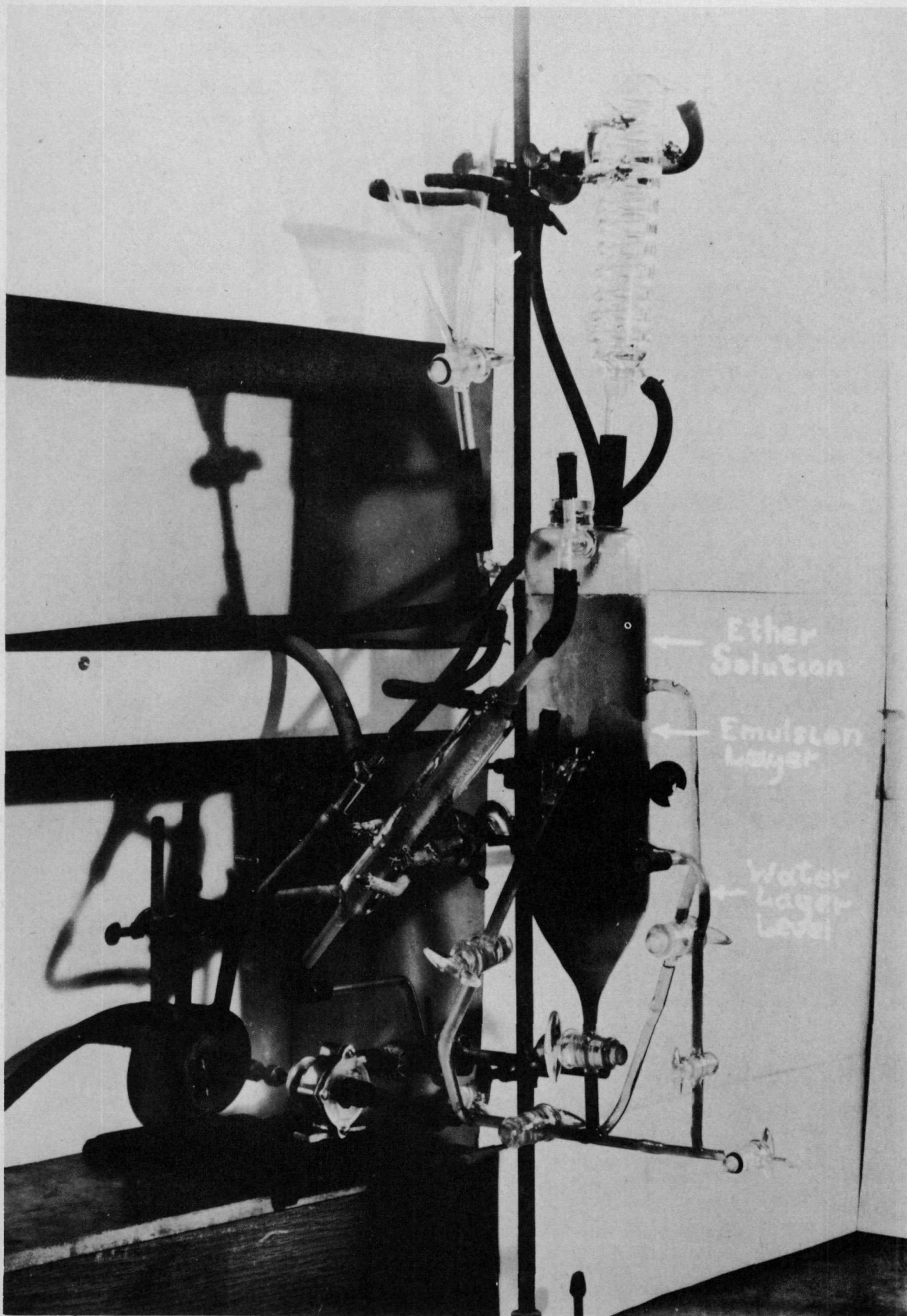


Fig. 3--A settled emulsion.

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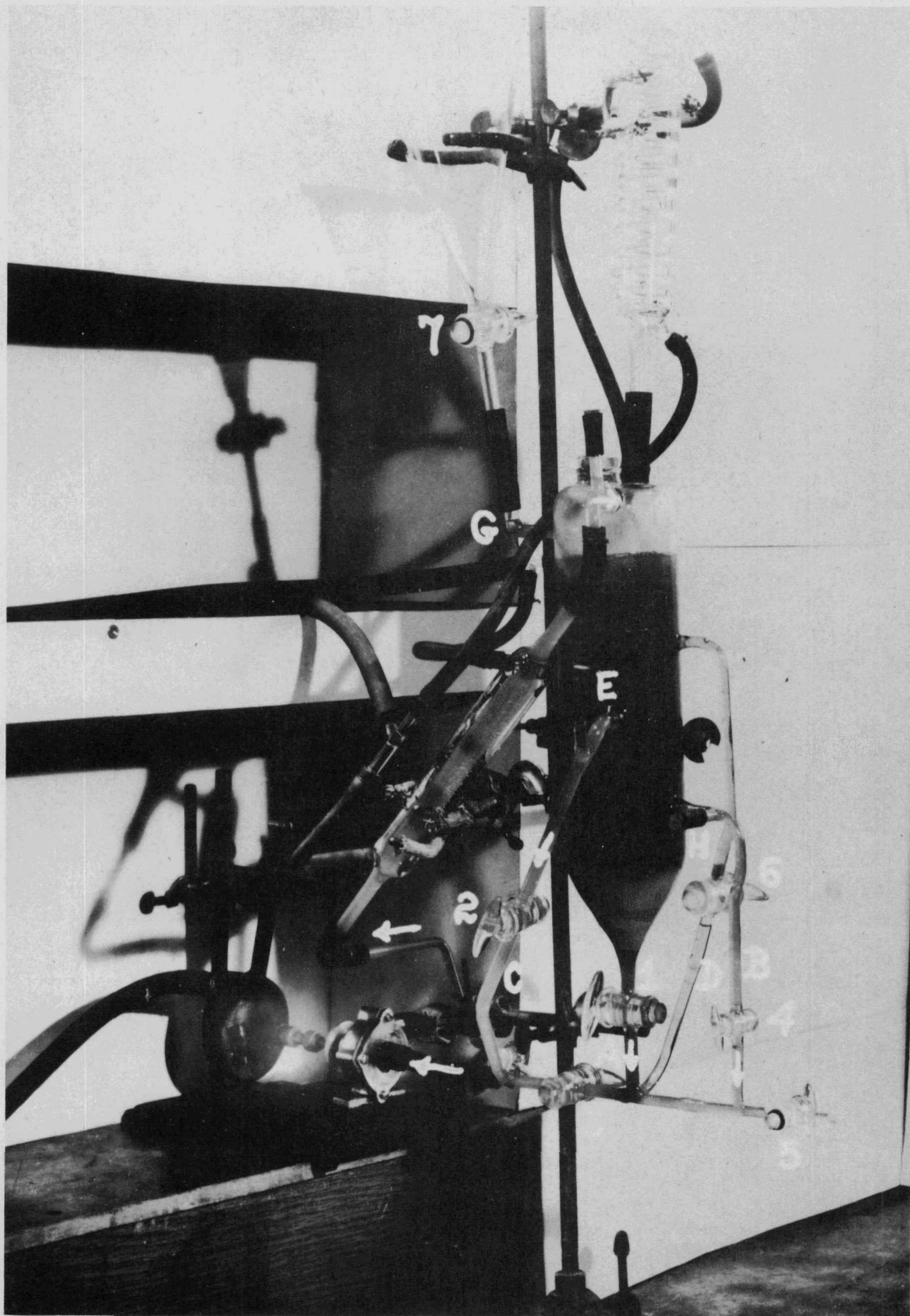


Fig. 4--Breaking an emulsion.

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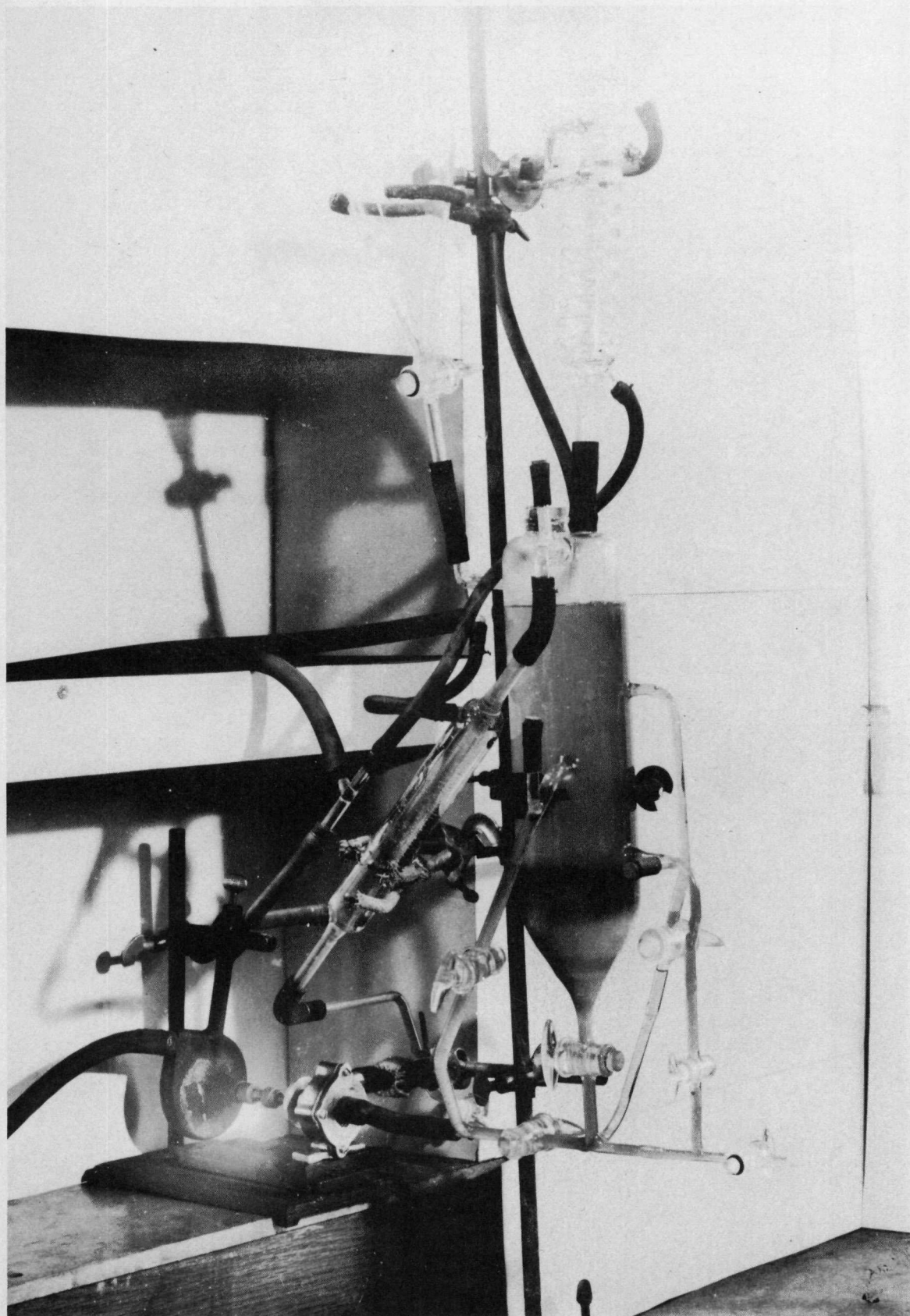


Fig. 5--Complete separation of layers.

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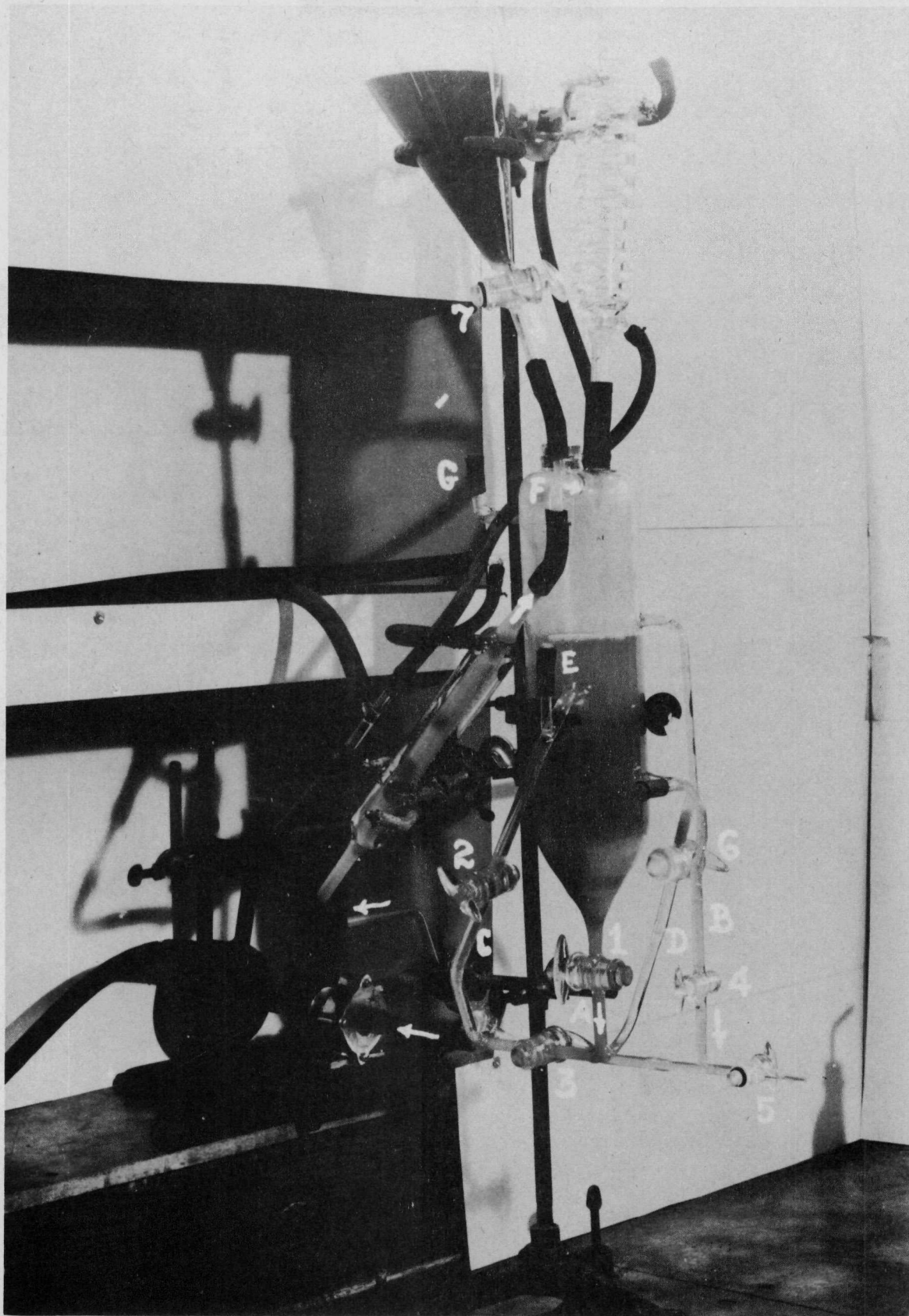


Fig. 6--Adding molten liquor with Set-Up II.

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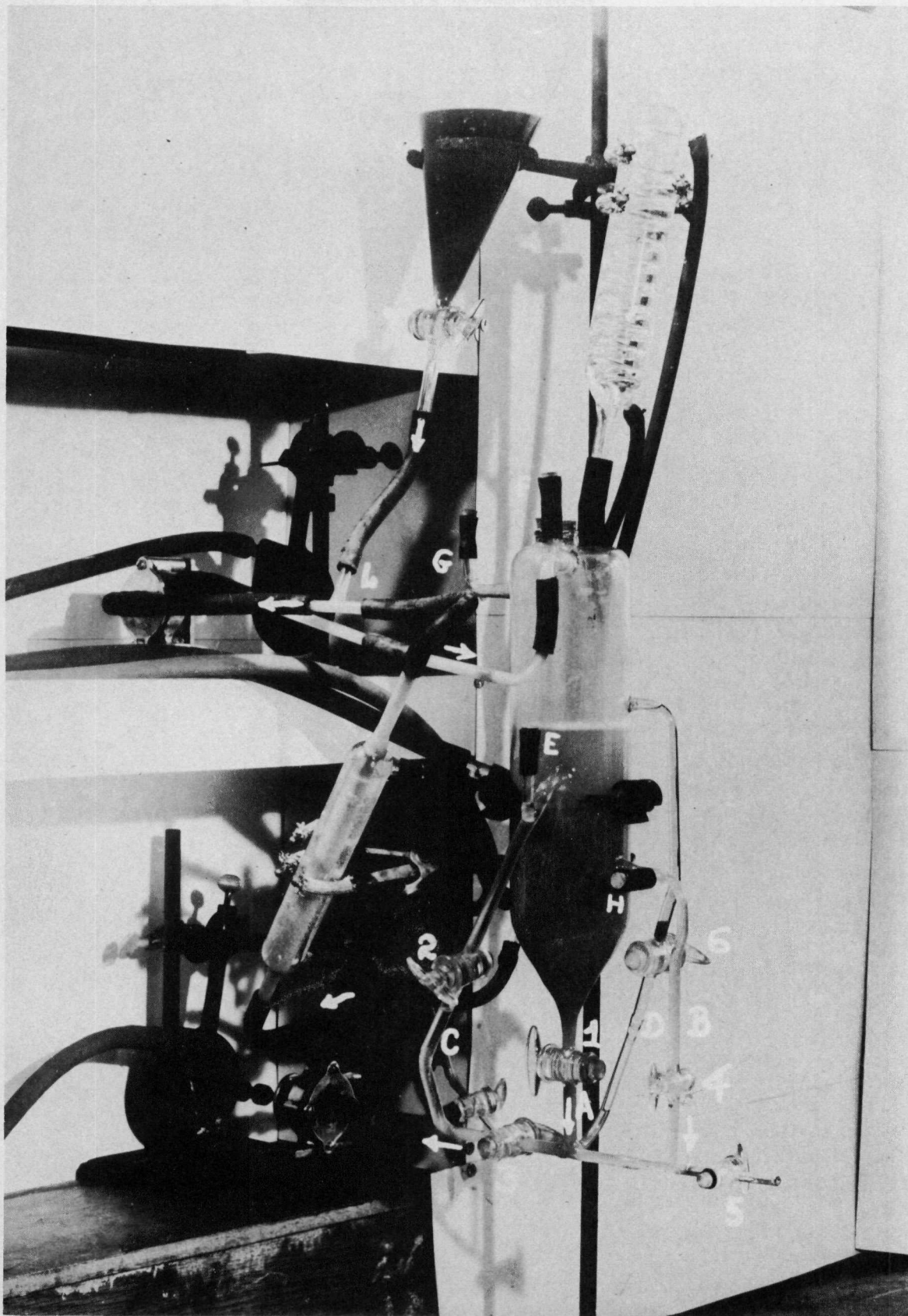


Fig. 7--Adding molten liquor with Set-up III.

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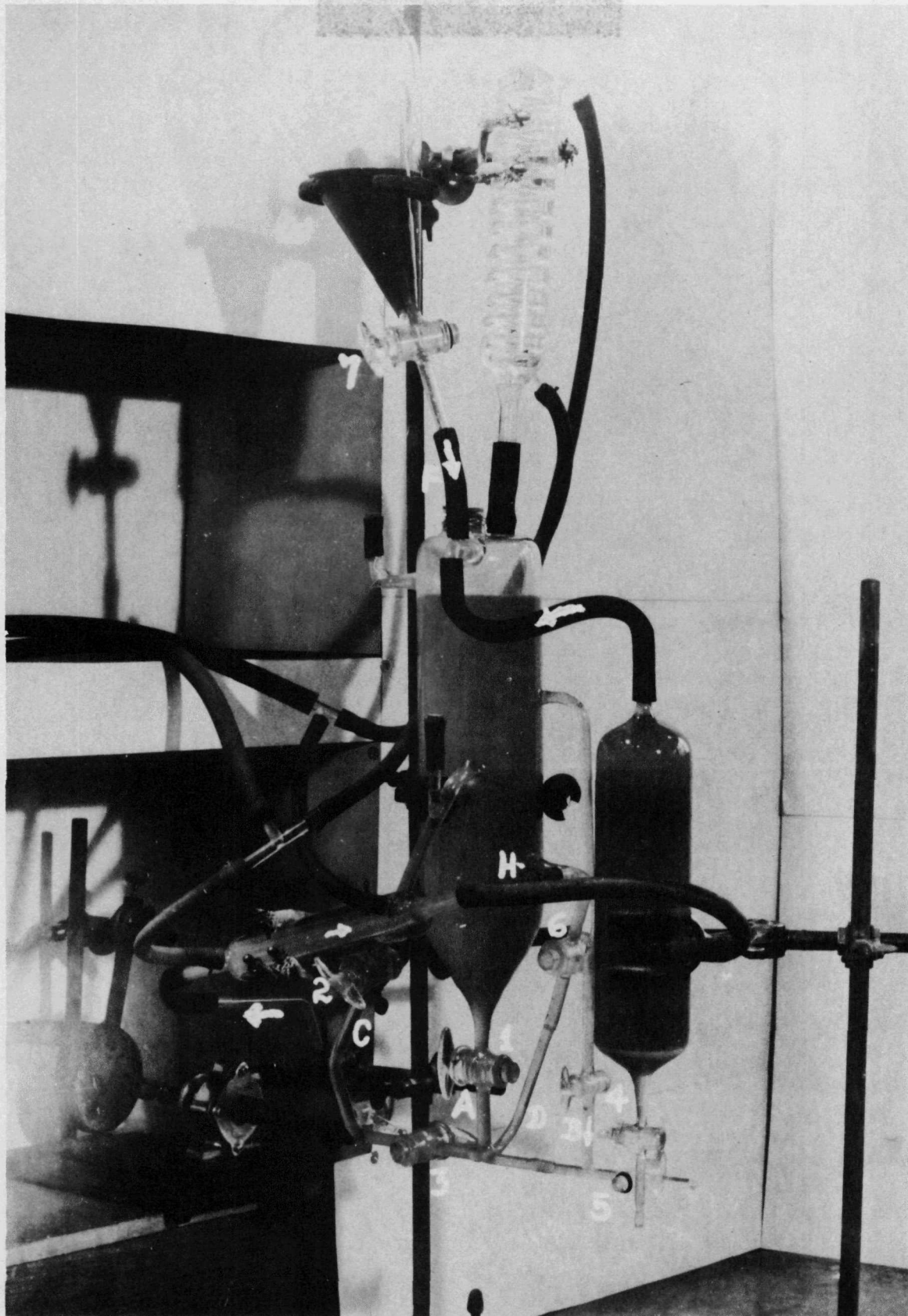


Fig. 8--Separation of water layer in auxiliary decanter.



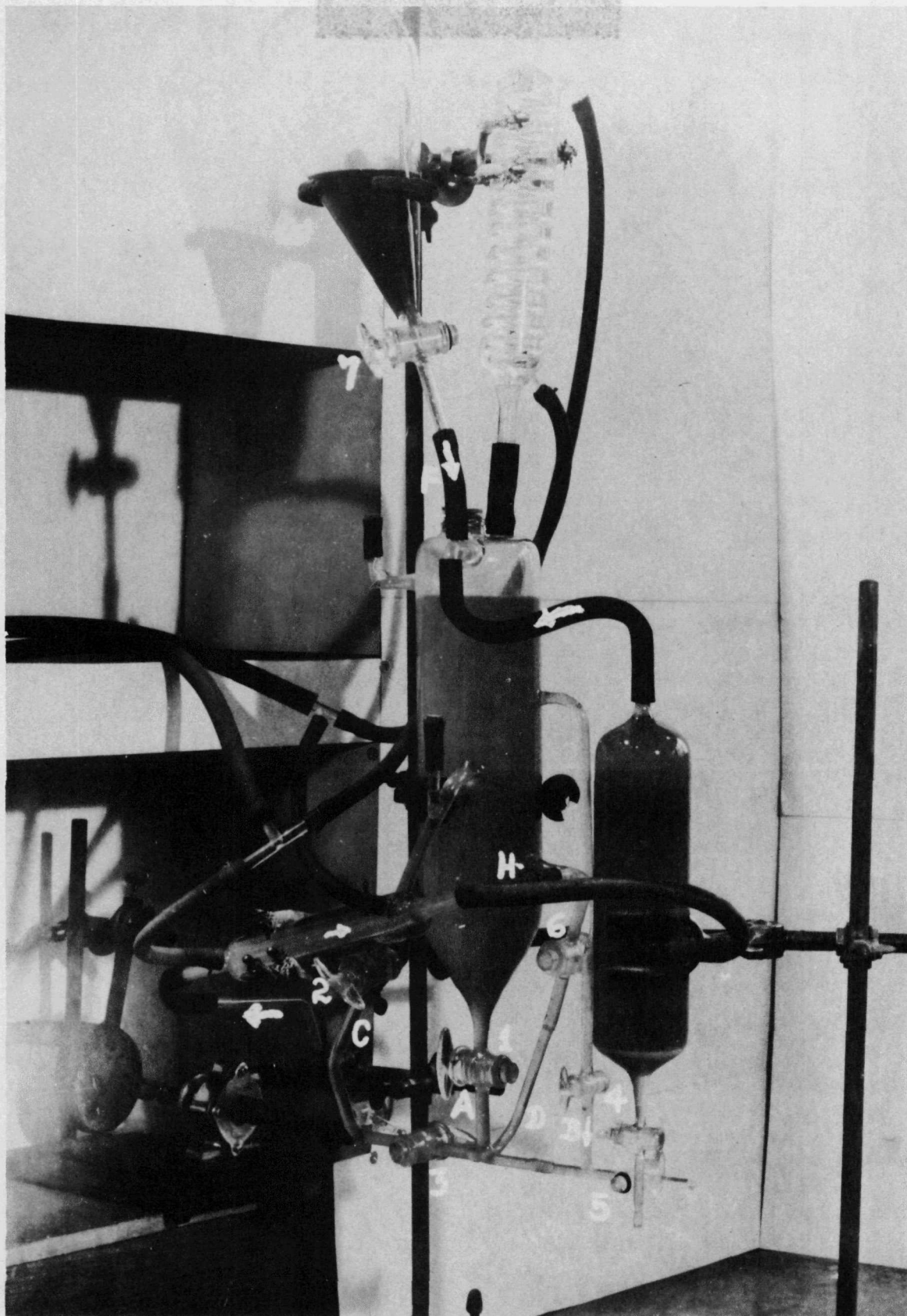


Fig. 8--Separation of water layer in auxiliary decanter.



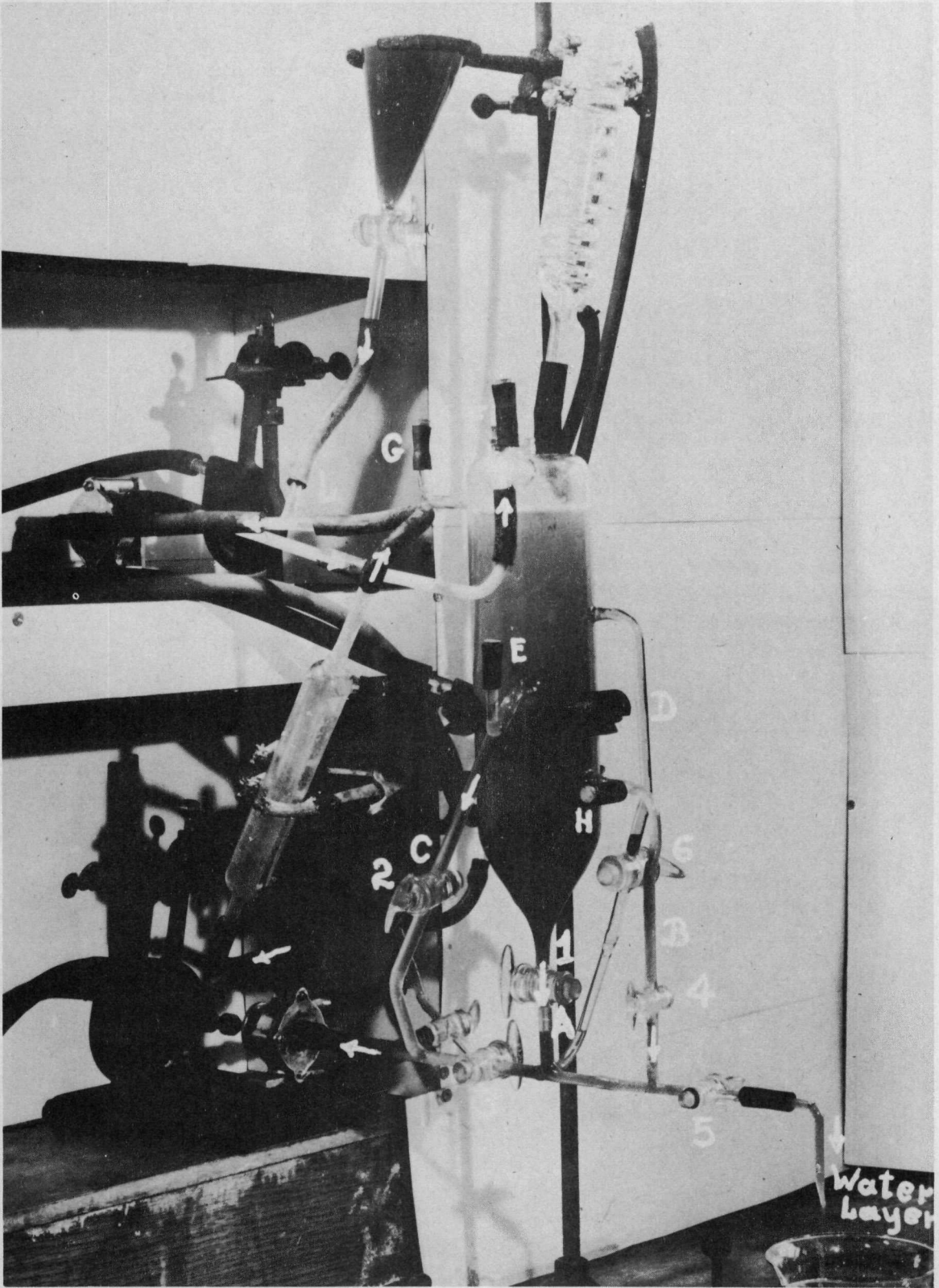


Fig. 9--Separation and continuous drainage of water layer in extractor.