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CONCENTRATION OF LOW MOLECULAR WEIGHT ALIPHATIC OLEFINS FROM OLEFIN-PARAFFIN MIXTURES BY ABSORPTION IN $AgNO_3$ SOLUTION, ESPECIALLY THE CONCENTRATION OF BUTYLENE FROM BUTYLENE-BUTANE MIXTURES

Whereas butylenes are only slightly absorbed in copper and mercury salt solutions, it was found that the solutions of silver salts, especially a saturated 50% silver nitrate solution, showed good absorption for butylene. In Figures 1 and 2 are shown the solubilities of ethylene, propylene and butylene in 50% $AgNO_3$ solution, in ammoniacal cuprous carbonate solution (so-called "plant solution" of the hydrogen purification) and in the ethanolamine-cuprous nitrate solution which up to now represented the most efficient absorption solution. The data in Figures 1 and 2 are taken from reports of other members of the staff of I. G., Leuna.

Whereas 50% $AgNO_3$ solution is the best solvent for α-butylene, the copper solutions preferentially absorb ethylene. The absorption capacity of $AgNO_3$ solution for isobutylene, β-butylene, propylene and ethylene in various concentrations forms a family of curves and it can be clearly seen that isobutylene shows higher solubility as compared to β-butylene whereas propylene is more soluble than ethylene. The absorption of propylene, isobutylene and n-butylene in ethanolamine-cuprous nitrate solution decreases strongly in comparison to ethylene. An accurate comparison of both solutions with respect to their absorption of related gaseous olefins cannot be made from the data in Figures 1 and 2 because the temperature in the experiments with silver nitrate solution was 36-37°F., whereas that of the copper solution was about 68°F. Figure 3 shows a comparison of the solubility in 50% silver nitrate solution and ethanolamine-cuprous nitrate solution under the same conditions (68°F., atm. pressure). The copper solution absorbs only ethylene in significant quantities, whereas the silver solution shows high absorption for all olefins tested.

Figure 4 shows the solubility of ethylene in 50% silver nitrate solution at 32°F. and 68°F. in relation to the partial pressure of ethylene. The data on the solubility of ethylene in cuprous nitrate-ethanolamine solution at 68°F. are again shown in this figure.

It was found in these experiments that at decreasing temperature and high ethylene concentration, a crystallized silver nitrate-ethylene compound precipitates out as white crystals.

The following conclusions can be drawn from Figures 1 to 4: Provided it is possible to combine the good solvent properties of the silver nitrate solution with high absorption rate and provided that the technique of continuous operation using such a valuable wash solution is mastered, absorption in $AgNO_3$ solution should be of general applicability for the separation of olefins and paraffins and should be more effective than washing with copper solution. For the separation of butane and butylene, the silver solution shows definite advantages.

Laboratory Experiments on Continuous Absorption of Gaseous Butane-Butylene Mixtures in 50% Silver Nitrate Solution.

Previous reports have dealt with wash experiments with silver nitrate solution which were carried out in the laboratory in glass columns filled with glass beads and in a small laboratory Ströder washer of a capacity of 22.6 cubic inches. About two gallons of a 50% silver nitrate solution per hour was passed through a glass column of a height of 1.3 feet and a diameter of 0.75 inches. A second column of the same height and a diameter of 1.5 inches was completely filled with silver nitrate solution which was continually renewed at the rate of 1 to 1.3 gallons per hour. The operating temperature was 36 to 37°F. The gas to be washed contained about 20% β-butylene and 80% n-butane. In the packed column through which silver nitrate solution was continually passed, the absorption of butylene was 2.3 volumes (measured at 68°F.) per volume of silver nitrate solution at a through-put rate of 11.5 volumes of gas mixture per volume of silver nitrate solution, a residence time of 10 seconds and a gas velocity of 3.9 inches per second. In the column filled with solution, the absorption of butylene amounted to 4 volumes of butylene gas per volume of silver nitrate solution at a through-put rate of 20 volumes of gas per volume of liquid and a residence time of 9 seconds at a gas velocity of 0.9 inches per second. Since the maximum solubility of 20% β-butylene in 50% silver nitrate solution is 12.5 volumes per gas, the efficiency of absorption in the first case is 18.4%, whereas in the second case it is 32%. Best washing results were obtained in the Ströder washer. At a through-put rate of 30 volumes of gas mixture per volume of silver nitrate solution, a residence time of 9 seconds and a gas velocity of 1.97 inches per second, 6.2 volumes of β-butylene gas were absorbed per volume of silver nitrate solution, corresponding to an efficiency of 50%. With practically complete absence of butylene in the butane in all cases, butylene of a purity of 98 to 99% was obtained.

Pilot plant runs were carried out continuously in a Ströder washer of a capacity of about 4 gallons solution and 1.9 cubic feet of gas. The results obtained were somewhat less favorable than those obtained on the laboratory scale. In an estimation of the probable cost of production of 97 barrels of butylene a day from a butylene-butane mixture containing 20% of butylene, the solution obtained in the Ströder washer was assumed to contain 4 volumes of butylene gas per volume of silver nitrate at a temperature of 50°F. This corresponds to an efficiency of 50% since a maximum of 8 volumes of butylene gas per volume of silver nitrate solution are absorbed at 50°F. from a mixture containing 20% butylene. Eleven hundred ninety (1,190) gallons of silver nitrate solution equal to 2.47 tons of silver were assumed to be required for filling the apparatus. The desorption of the absorbed butylene was carried out under vacuum at 50°F. and 10 mm. Hg.

Figure 5 shows a laboratory apparatus for the continuous absorption of olefins from a mixture of olefins and paraffin.

The apparatus consists essentially of a jacketed absorption column of 4.9 feet height and 1.2 inches diameter which is packed with 5 mm. (0.2 in.) Raschig rings, a butylene regenerator with a capacity of 2 liters provided with steam heat (V_2A coil) and nitrogen agitation, a small V_2A cooler (water) and a second cooler operated with brine. The silver nitrate solution passes from a measuring vessel of 500 cc. capacity into the head of the absorption column. After the desired amount of silver nitrate solution has entered the column, the liquid level is maintained by pumping in fresh silver nitrate solution by means of a V_2A gear pump at such a rate that a constant volume of silver nitrate in the column is guaranteed. The silver nitrate solution is freed from absorbed butylene

at about 176°F. using nitrogen as flushing gas. The regenerated solution is cooled, first by water and then by brine, and returned to the measuring vessel by means of the pump mentioned above. The butylene is separated from nitrogen by low temperature distillation. The maximum permissible through-put through the column at a temperature of 36 to 37°F. was 16 liters silver nitrate solution and 200 liters of gas per hour (measured at 68°F. and 760 mm. Hg). (This corresponds to 4.2 gallons of silver nitrate solution and 7.2 cubic feet of gas.) Under these conditions (12.5 volumes of gas per volume of silver nitrate solution), a 22% mixture of butane and butylene could be extracted giving a residual concentration of 0.4% butylene in the exit butane. This corresponds to an efficiency of about 22.5%. According to laboratory work by others, a somewhat higher through-put rate should have been expected; however, it was not possible to obtain satisfactory operation with a higher through-put because of carry-over of the silver nitrate solution. The butylene obtained had a purity of 97 - 99%. Besides synthetic mixtures, a butane-butylene mixture obtained by the dehydrogenation of n-butane in the plant was also processed. The distillation curve of this dehydrogenation butylene of a purity of 98% is shown in Figure 6.

It can be seen that the butylene from dehydrogenation consists of about 43% α-butylene and 57% β-butylene.

Continuous extraction experiments with mixtures of butane and α-butylene gave better results because of the higher absorption of α-butylene by the silver nitrate solution. In this case, about 25 volumes of gas per volume of silver nitrate solution could be processed and yielded an exit gas which was practically free from butylene. This means that the through-put was about twice that of β-butylene.

Equilibrium Studies with 50% Silver Nitrate Solution and Liquid Mixtures of Butane and Butylene.

Studies of the absorption of butylene from gas mixtures containing only a small concentration of butylene were undertaken because the butane-butylene mixture obtained by dehydrogenation contained only 20 to 25% butylene and, on the other hand, in counter-current absorption the butylene concentration in the butane can assume values from 20 to 25% down to 0 to 1%.

These experiments were carried out with liquid butane-butylene mixtures since the mixture of butane and butylene from the butane dehydrogenation is obtained in liquid form. Operation in the liquid phase has the advantage that the absorption apparatus can be of smaller dimensions and the volume of silver nitrate solution can be decreased. It also permits to operate at lower temperatures which results in higher absorption. At 32°F. condensation would take place when gaseous butane-butylene mixtures are washed.

Equilibrium determinations were carried out in the laboratory in glass pressure bottles of a capacity of 0.75 liters. One hundred (100) cc. of 50% silver nitrate solution and 400 cc. of a liquid butane-butylene mixture were shaken for 10 minutes, the mixture was allowed to settle and after separation the butylene content was determined in both layers. The relation of butylene absorption and temperature is shown in Figure 7, whereas Figure 8 shows the butylene absorption in relation to the butylene concentration in the butane. Both Figures 7 and 8 show that absorption increases with decreasing temperature and the practically linear curve indicates that the butylene absorption in the region investigated closely follows Henry's Law. When the liquid hydrocarbon mixture and silver nitrate solution was shaken by hand for 1 minute, the absorption values

obtained were as high as those found when shaking was continued for 10 minutes. This indicates that the absorption rate is high even in the region of low butylene concentration.

To obtain design data for a commercial unit, experiments were carried out using a flow system. The operating temperature was chosen as 32°F, since lower temperatures would lead to the separation of a solid precipitate from the silver nitrate solution as indicated by Figure 9. The apparatus used is shown in Figure 10. It consists mainly of a 50 cc. flask with a stirrer and a separator of about 500 cc. capacity. Mixer and separator are both kept in a cooling bath. The experiments were carried out at 32°F. with a residence time of 5 seconds and a volume ratio of silver nitrate solution to β-butylene mixture of 1 : 4. The butylene concentration in the butane-butylene mixture was varied and the concentration of the gas in the silver nitrate solution was also varied. The results of these tests are shown in Figure 11. The amounts of butylene absorbed by 100 cubic centimeters of silver nitrate solution, in addition to whatever butylene may be present in the silver nitrate solution, are plotted on the ordinate, whereas the abscissa represents the percent of butylene in equilibrium with the silver nitrate solution leaving the system. The data above the abscissa represent the butylene absorbed by the silver nitrate solution, whereas the data below the abscissa represent the butylene given off from the silver nitrate solution to butane. The diagram indicates clearly that absorption and desorption practically follow Henry's Law. The fact that the curves are straight lines, as well as a comparison with the isotherms at 32°F. given in Figure 8, indicate that at a residence time of 5 seconds in the flow system static equilibrium is reached at all the concentrations studied in these experiments.

The results in Figure 11 are important for the technical operation of this process since the apparatus used can be considered as one stage of a countercurrent washer with an efficiency of 100% at a residence time of 5 seconds. It is entirely possible that lower residence times will be sufficient, provided that intensive emulsification can be obtained.

Liquid phase operation, high efficiency, short residence time in the mixer, as well as short settling time in the separator, result in a decrease of the size of the apparatus and require a smaller quantity of the valuable silver nitrate solution to circulate in the unit. Studies of the settling time required, especially for the silver nitrate phase, have been carried out and the purity of the butylene from the silver nitrate solution for various settling times after intensive emulsification were obtained. The results are given in Figure 12. The optimum butylene purity was obtained at a settling time of between 15 and 20 seconds. Below 10 seconds the butylene purity decreases because of the presence of butane in the silver nitrate phase. The settling times necessary for the butane phase were not determined but are of a similar magnitude. Longer residence times of the butane phase in the settler for the separation of last traces of silver nitrate solution do not mean a higher requirement of silver nitrate solution which is of importance. Foaming, which is frequently observed in the technical washing of gases, has not been found in these small-scale experiments and was also not observed in the pilot plant experiments which will be described below.

Figure 11 indicates that the butylene absorbed by the silver nitrate solution can be removed from the solution by means of butane. This means that the system is in true reversible equilibrium which, at a given temperature, is only dependent on the concentrations.

This finding is important if the silver nitrate absorption should be used for the separation of butane from butylene in the alkylation plant. If, prior to alkylation, butylene is separated from n-butane by washing with silver nitrate, the butylene absorbed by the silver nitrate solution can be liberated by passing isobutane into the solution and the mixture of isobutane and butylene so obtained is passed to the alkylation reactor. Absorption and desorption can be carried out at the same temperature and pressure so that no energy for the liberation of butylene is required for the operation of the silver nitrate absorption. Otherwise, the energy requirements for the liberation of butylene by heat would be somewhat large since the large amount of silver nitrate solution circulated per unit of time must be heated from 32 - 212°F. and afterwards cooled again to 32°F. Liberation of butylene by vacuum and heat would probably be equally disadvantageous economically. Since alkylation also is carried out 32°, only the specific heat for cooling and heating of the n-butane portion would be required in case that desorption of butylene is being effected by means of isobutane. Energy, of course, is required for circulation of the silver nitrate solution.

The desorption of butylene can also be carriedout with other hydrocarbons - for instance, hexane and octane. With these hydrocarbons the same results were obtained as with isobutane. However, in this case, the butylene would have to be separated by distillation from the higher hydrocarbons and this certainly would affect the economics of the process.

Calculation of a Stepwise, Counter-Current Extraction with 50% Silver Nitrate Solution Operating at 32°F. for Beta-Butylene.

Using the data given in Figure 11, the number of stages was calculated by the method of T. G. Hunter - "THE SCIENCE OF PETROLEUM", volume 3, page 18 - "Theoretical Principles of Solvent Extraction". The results are shown in Figures 13 to 17. The number of stages calculated are plotted on the ordinate, whereas various other conditions are plotted on the abscissa. The number of theoretical stages can be considered equal to the practical ones if, in each stage, an efficiency of 100%, i. e., static equilibrium - is reached.

Figure 13, which shows the relation of the number of stages to the volume ratio of butane-butylene and silver nitrate solution, indicates that it is advantageous to operate with a volume ratio of 1 : 4 to 1 : 6, corresponding to 3 - 7 stages. Below the ratio of 1 : 4, the number of stages increases rapidly so that at a ratio of 1 : 3.2 it is already infinite. The advantages obtained with a volume ratio above 1 : 6 are only slight.

Figure 14 shows the relation of the number of stages and the butylene content in the exit n-butane. If the concentration of butylene in the butane is permitted to be 3% instead of 1%, the number of stages required decreases from 4.5 to 2.5.

Figure 15 shows the relation of the number of stages to the butylene content in the silver nitrate solution for the case that the butylene concentration in the exit butane is 1 - 2%. The number of stages increases with increasing concentration of butylene in the silver nitrate solution and this increase in the number of stages becomes smaller if less stringent requirements are made for the concentration of butylene in the exit butane. Figure 16 shows the practically linear relationship of the number of stages and the butylene content in the n-butane feed. Increase of the butylene content from 15 to 30% in the feed increases the number of stages required by only 0.5. Figure 17 shows the relation of the number of stages in the desorption period as dependent on the volume ratio

of the silver nitrate solution and butylene to isobutane. Similar to the absorption, a large increase in the number of stages is noted below a volume ratio of 1 : 0.5, whereas above 1.05 the number of stages is only little decreased by increasing the amount of isobutane added.

The following operating conditions appear to be most advantageous for using silver nitrate absorption as a process step in alkylation.

Absorption.

Volume ratio of butane and butylene to silver nitrate solution 1 : 5; number of stages - 5; concentration of butylene in inlet gas - 22.6%, concentration of butylene in the silver nitrate solution charged - 0.3% by vol.; concentration of butylene in exit gas - 2%, concentration of butylene in silver nitrate solution drawn off - 4.42% by vol.

Desorption.

Volume ratio of silver nitrate solution, plus butylene to isobutane 1 : 0.45; number of stages - 4; concentration of butylene in $AgNO_3$ solution charged 4.42% by vol.; concentration of butylene in the isobutane 0.5%, concentration of butylene in exit isobutane 8.4%; concentration of butylene in the silver nitrate solution 0.3% by vol.

These conditions have been calculated for the case that the butylene consists entirely of β-butylene; however, according to Figure 6, it can be assumed that the dehydrogenation butylene consists of about 43% α- and 57% β-butylene and this would result in better operation of the silver nitrate absorption than assumed above. Figure 18 shows the absorption of a mixture of α- and β-butylene in 50% silver nitrate solution. Experimental work is required on the desorption of a mixture of these two butylenes.

When the desorption is carried out by means of higher hydrocarbons, a mixture of hydrocarbons containing 7 - 8.5% butylene would have to be distilled to a residual butylene concentration of 0.5% in the hydrocarbons. It is doubtful whether under these conditions a saving in energy would result from the use of hydrocarbons for desorption instead of heat and vacuum.

Pilot Plant for Silver Nitrate Extraction.

In order to decide what materials could be used for the construction of silver nitrate extraction units, the following materials were tested for their resistance against 50% silver nitrate solution: V17F, VK17F, V_2A and V_4A, Vinidur (Igelit), Oppanol OG, Oppanol ORG, iron coated with Phenytal lacquer and Haveg. Test pieces of these materials were exposed at room temperature to 50% silver nitrate solution. All materials, with the exception of Haveg, did not change their appearance after 45 days of contact and also did not affect the properties of the silver nitrate solution. The silver nitrate which was in contact with Haveg turned brownish after 7 days. In the course of 45 days a silver layer had deposited on the Haveg test piece and the solution showed brown flocks. The non-metallic materials mentioned have a disadvantage as compared to the special steels tested insofar that on prolonged contact with liquid butane they show swelling. Results with boiler steel and special steels are given in the following table:

(over)

Material	50% $AgNO_3$ Solution	50% $AgNO_3$ Solution + 2% HNO_3	
	Increase in weight, mg/cm^2	Corrosion, mm/year	
boiler steel	+ 0.15	0.075	test pieces spotty
N_5	+ 0.10	0.010	
N_6	+ 0.20	0.000	
V_6M	+ 0.26	0.075	test pieces unchanged
$V_{17}F$	+ 0.27	0.000	

7 days exposure, 104°F.

No change in color of the solution

On the basis of the corrosion tests, the pilot plant was built of V_2A.

Design.

Figure 19 shows the flow diagram of the pilot plant as finally adopted.

It consists of 10 stages, 5 stages for absorption and 5 stages for desorption. Each stage consists of a contactor of a capacity of 0.26 gallons provided with a stirrer and connected by means of an overflow with a separator of a capacity of 0.8 gallons. Both the mixer and the separator are placed in pans through which brine is circulated. The stirrers are driven by a common shaft.

Regenerated silver nitrate solution is pumped from the surge tank 1 through an orifice into the separator 4 and passes through the 5 absorption stages into the surge tank 2. From there the fat silver nitrate solution is pumped through an orifice into the separator 3 and is passed into the 5 desorption stages and returned to surge tank 1. The butane containing butylene is pumped from the surge tank 5 through an orifice into a preliminary cooler and then passes through the 5 absorption stages from where it flows into the separator 4 which it leaves to flow into a storage tank maintained at constant pressure by means of nitrogen. The isobutane used for desorption is pumped from the surge tank 6 through an orifice through a preliminary cooler and passed through the 5 desorption stages, leaving the desorption unit through the separator 3 and is stored in a tank which is also maintained at constant pressure by means of nitrogen. Both storage tanks are not shown in the diagram. All lines of the silver nitrate absorption unit are well insulated.

Operation and Results.

The unit was operated with 50% silver nitrate solution which was stabilised by the addition of 2% nitric acid. The addition of nitric acid is without effect on the absorption and desorption properties of the solution. A total of 18.5 - 21 gallons of solution was circulated. The largest portion of the solution was in the surge tanks 1 and 2. A mixture of isobutylene and n-butane containing 25 - 30% isobutylene was used for the experiments. Isobutylene was used

because it could be easily obtained; its solubility lies between that of α- and β-butylene. For desorption, isobutane was used which had been washed with sulphuric acid and caustic and contained only 0.4% butylene. The stirrers operated at 500 r. p. m. The temperature in the agitators varied between 28° and 68°F. The many stuffing boxes on pumps and stirrers and the belt for the operation of the stirrers caused frequent interruptions so that continuous operation could not be reached. The longest period of operation without interruption was 12 hours and the results of this run are given as follows: The unit operated with a through-put rate of 65 gallons of silver nitrate solution per hour, 13 gallons of a mixture of isobutylene and n-butane with an isobutylene concentration of 27% and 47.6 gallons of isobutane for desorption with an olefin content of 0.4%. Except for the starting period, the n-butane could be washed to a residual concentration of isobutylene of 0.6 - 2.2%; consequently, about 13 pounds of butylene were extracted per hour. This result could also be confirmed in other experiments and showed that it is in principal possible to carry out the separation of butane and butylene by means of silver nitrate solution.

The unit could not be operated at a higher through-put rate since the cross-section of the lines was too narrow so that at a higher through-put the back pressure of the silver nitrate solution became too high. Foaming of the solution was never observed. Samples taken from various stages during the run indicated clearly that the solution always separated completely and carryover in the various stages was never observed.

Silver nitrate was never detected in the butane leaving the unit so that silver losses need not be anticipated from this source. The silver nitrate solution which had been used in the unit for several months showed brown discoloration but when tested in a laboratory apparatus showed the same absorption efficiency as at the time when it was fresh. The brown discoloration is probably due to finely divided rust particles. No data were obtained on the overall silver losses in the unit.

Silver Nitrate Extraction in the Alkylation Process.

Calculations have been made on the quantity of butane to be vaporized and condensed for the manufacture of one barrel of alkylate with and without silver extraction. Figure 20 shows the material balance for the alkylation process using silver extraction; the calculations refer to the manufacture of 9 barrels of alkylate. The mixture of butane and butylene from the dehydrogenation after stabilization contained 22.6% butylene and entered the absorption unit as liquid, leaving it with a butylene content of 1.86%. After the addition of fresh n-butane from the debutanizer and recycle n-butane from the n-butane isobutane splitter of the alkylation, the combined n-butane is returned to the dehydrogenation with an olefin content of 2.4%.

Silver extraction of unstabilized butane-butylene mixtures is not feasible since the silver solution is noticeably reduced by hydrogen which results in the separation of silver. The butylene dissolved in the silver nitrate is liberated by recycle isobutane (from the head of the n-butane-isobutane column and from the bottom of the isobutane-propane separation) as well as, if required, by part of the direct-cooling butane from the alkylation; the liberated butylene is passed to the alkylation. The cooling butane represents a more than sufficient reservoir of butane for the liberation of butylene. However, it will be necessary to wash the butane from the alkylation with caustic or water in order to remove the SO_2. According to previous investigations, the amount of water in the butane which is in equilibrium with 50% silver nitrate solution at 32°F. is so small that

drying of the butane-butylene mixture after liberation from the silver nitrate prior to the introduction into the alkylation is not necessary, provided that a sufficiently long settling time of the butane is allowed.

The following table shows the amount of distillate, its purity and the reflux ratio, as well as the total quantity of butane to be evaporated for the manufacture of 1 barrel of alkylate with and without silver solution extraction.

	Butane Feed Preparation		Alkylate Debutanizer		Butane Splitter	
	Without $AgNO_3$ Extraction	With $AgNO_3$ Extraction	Without $AgNO_3$ Extraction	With $AgNO_3$ Extraction	Without $AgNO_3$ Extraction	With $AgNO_3$ Extraction
Amount of Distillate (lbs.)	163	170	1114	986	712	134
Purity	85%	73%	Free from C_5 and higher hydrocarbons		85%	71.7%
Reflux Ratio	1:9	1:3.5	1:0.4	1:0.4	1:5	1:2
Amount of Butane to be evaporated (lbs.)	1610	761	1560	1383	3565	405

According to the data shown in the table, the silver nitrate extraction saves the energy required to evaporate and condense 4,186 pounds of butane per barrel of alkylate. Since the mixture of hydrocarbons resulting from the dehydrogenation contained about 0.6% of butadiene, based on the total amount of butane and butylene present, the behavior of butadiene in the silver extraction is important. Butadiene is absorbed by the silver nitrate solution without forming a precipitate as in the case of copper solution. The absorption of butadiene corresponds approximately to that of α-butylene. It is important to note that butadiene can be desorbed with butane in the same way as butylene so that complications due to the retention of butadiene in the silver nitrate solution need not be expected.

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FIG. 1

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SOLUBILITY OF ETHYLENE, PROPYLENE AND BUTYLENE IN 80% $AgNO_3$ SOLUTION AT 86-87°F.

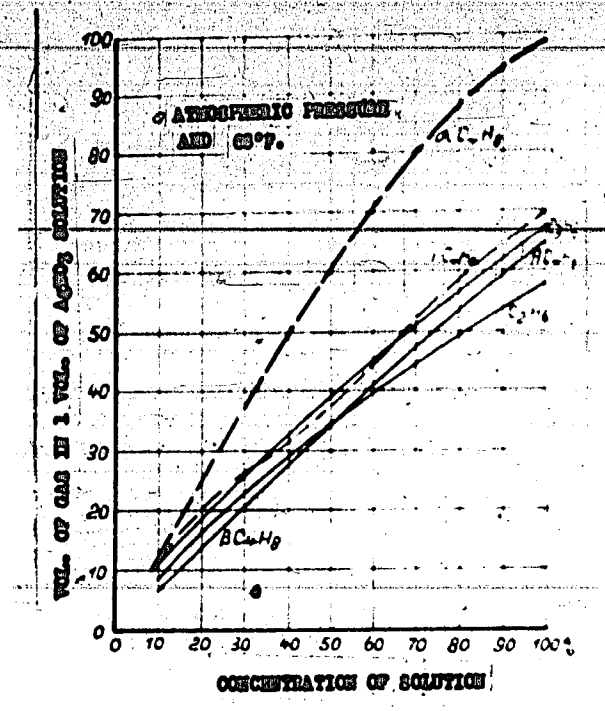

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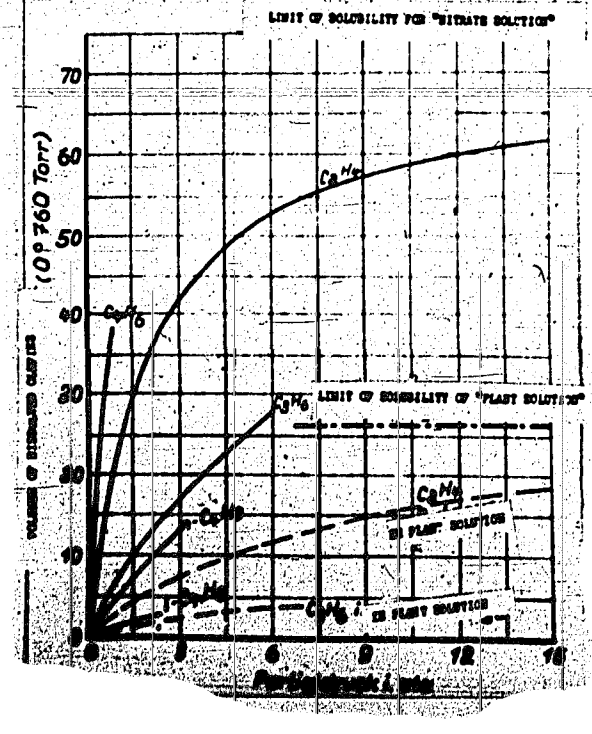
FIG. 2

SOLUBILITY OF GASEOUS OLEFINS IN CUPROUS NITRATE-ETHANOLAMINE SOLUTION AND PLANT CUPROUS CARBONATE SOLUTION IN RELATION TO PRESSURE AT 68°F.



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COMPARISON OF THE SOLUBILITIES OF ETHYLENE, PROPYLENE, α - ,β- AND ISO-BUTYLENE IN 50% $AgNO_3$ SOLUTION AND CUPROUS NITRATE-ETHANOLAMINE SOLUTION AT 68°F. AND 760 mm Hg.

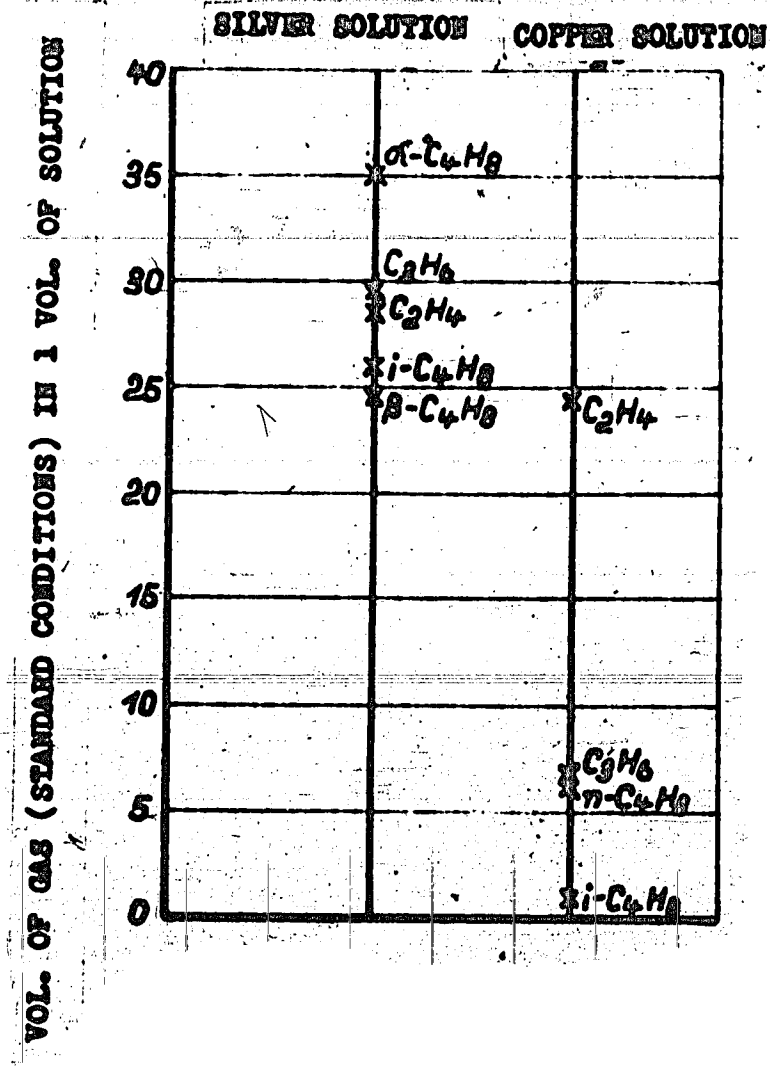

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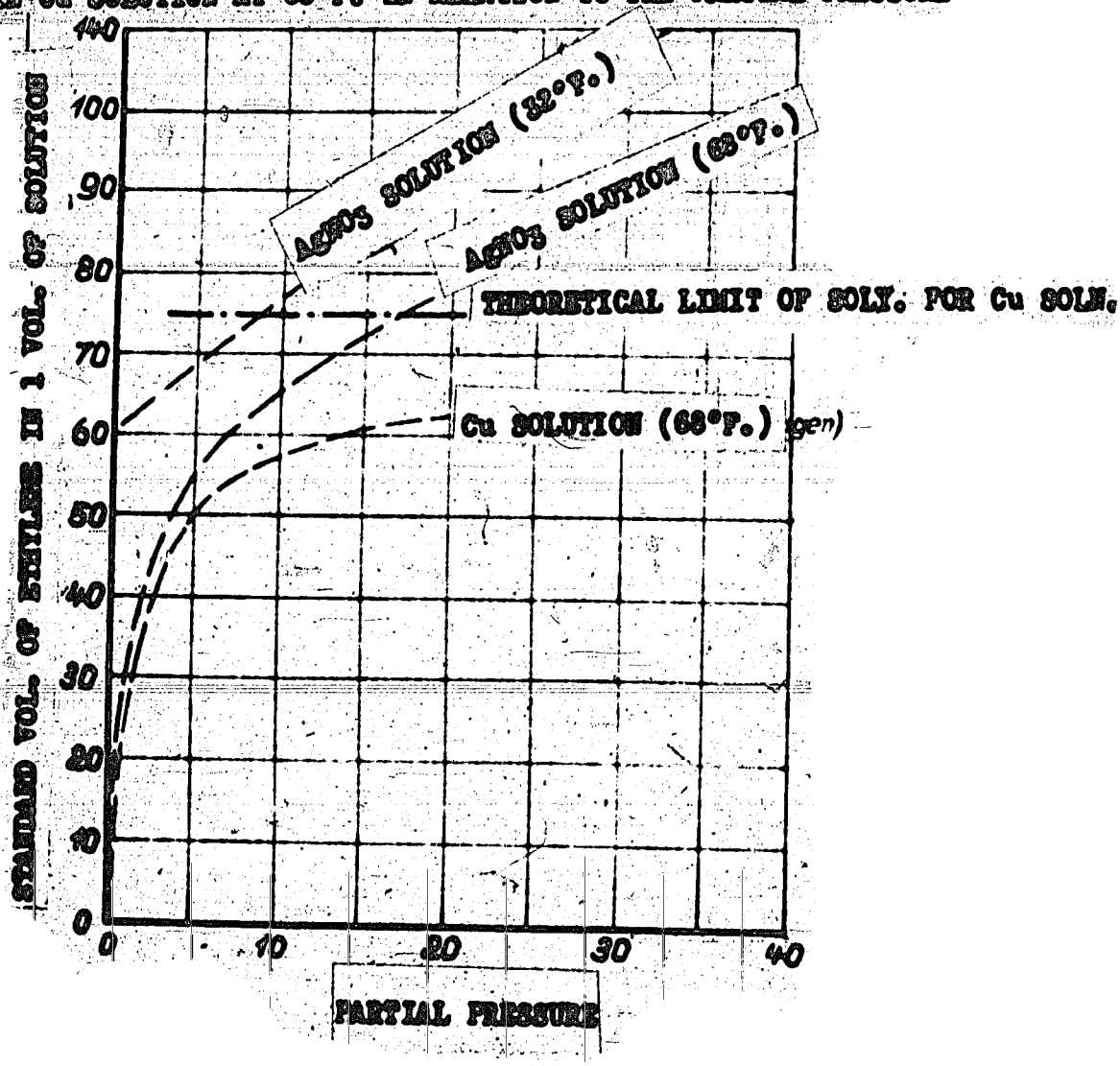
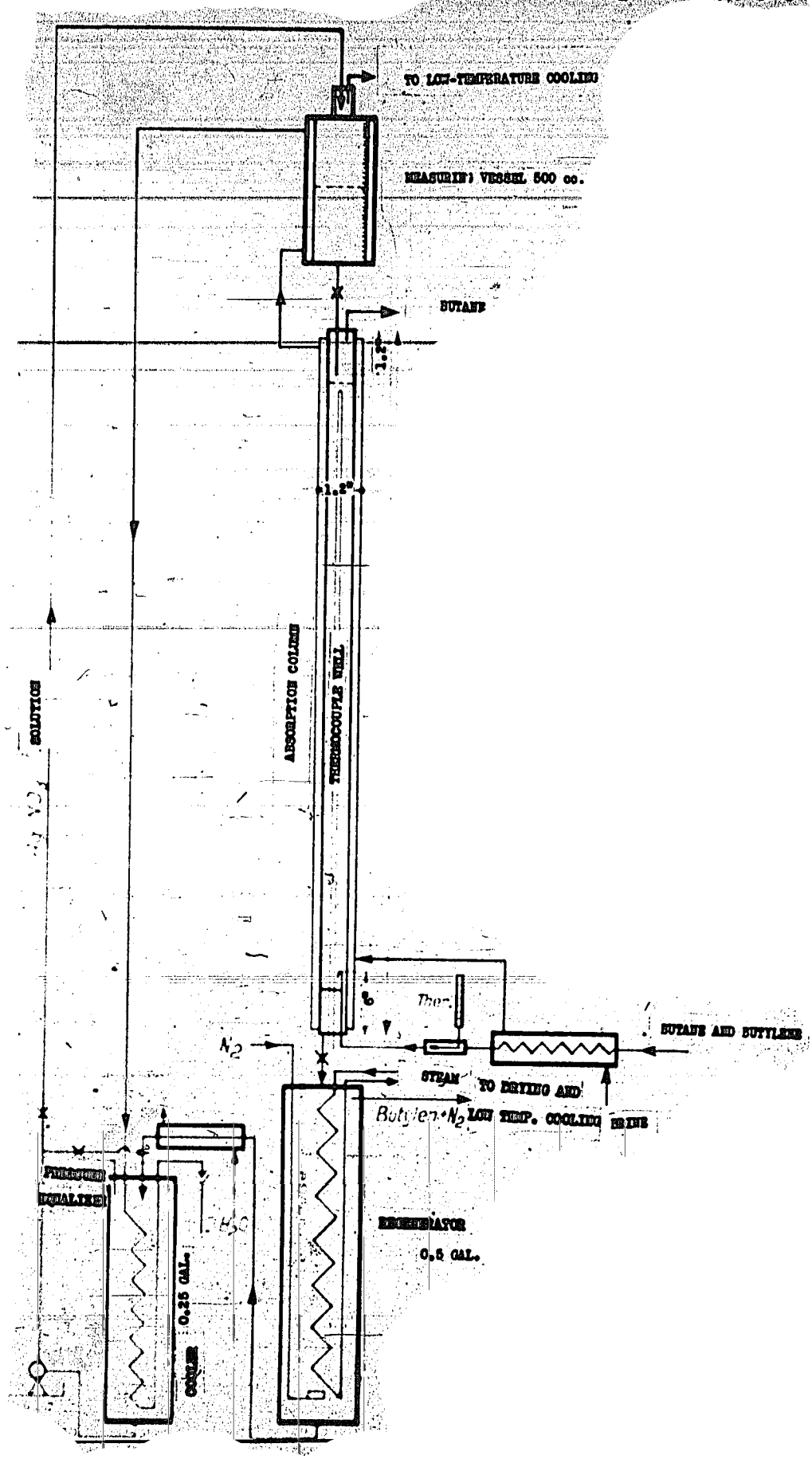
FIG. 4

SOLUBILITY OF ETHYLENE IN $AgNO_3$ SOLUTION AT 68°F. AND 32°F. AND IN Cu SOLUTION AT 68°F. IN RELATION TO THE PARTIAL PRESSURE




TO LOW-TEMPERATURE COOLING
MEASURING VESSEL 500 cc.
BUTANE
2.5°
1.2°
ABSORPTION COLUMN
THERMOCOUPLE WELL
SOLUTION
Thermometer
BUTANE AND BUTYLENE
N_2
STEAM
TO DRYING AND
Butylen+N_2
LOW TEMP. COOLING BRINE
PRESSURE EQUALIZER
REGENERATOR
0.5 GAL.
0.25 GAL.
COOLER

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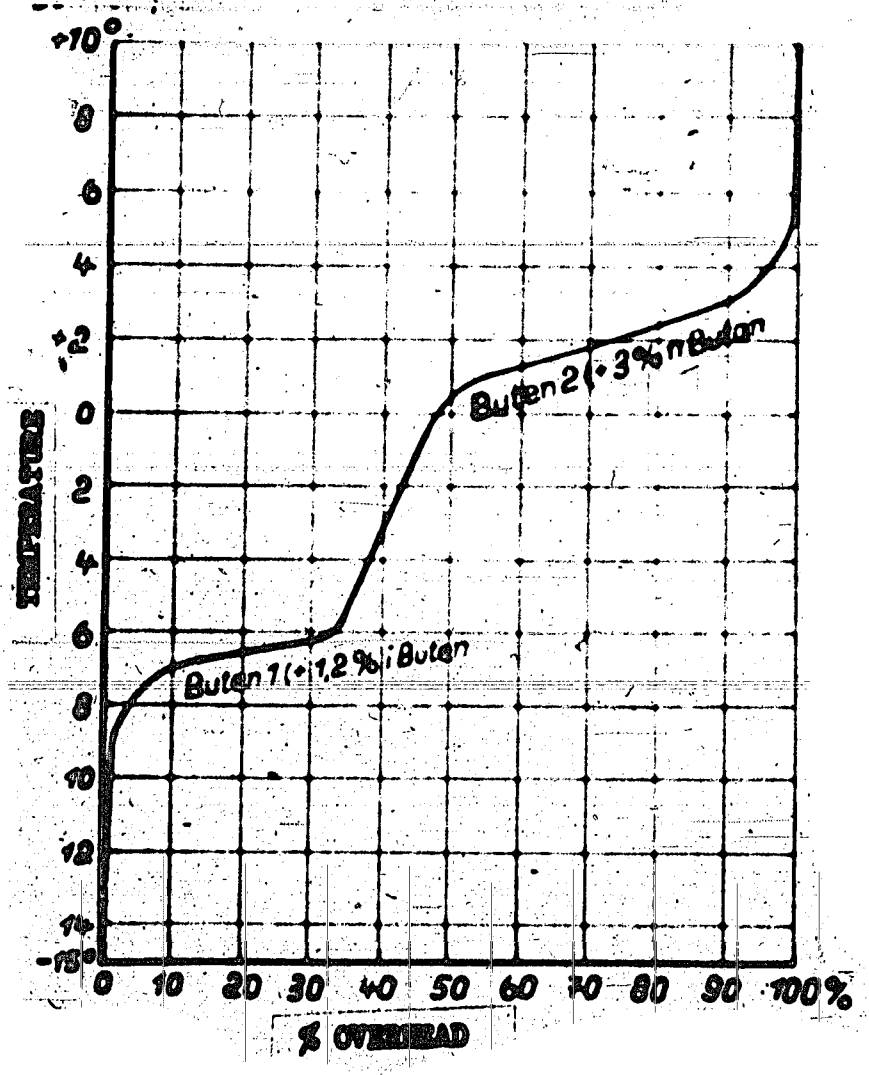
BOILING CURVE OF BUTYLENE (96%) MADE BY DEHYDROGENATION OF n-BUTANE AT 1076°F.
(DISTILLATION IN HOCH-HILDEBRATH COLUMN)



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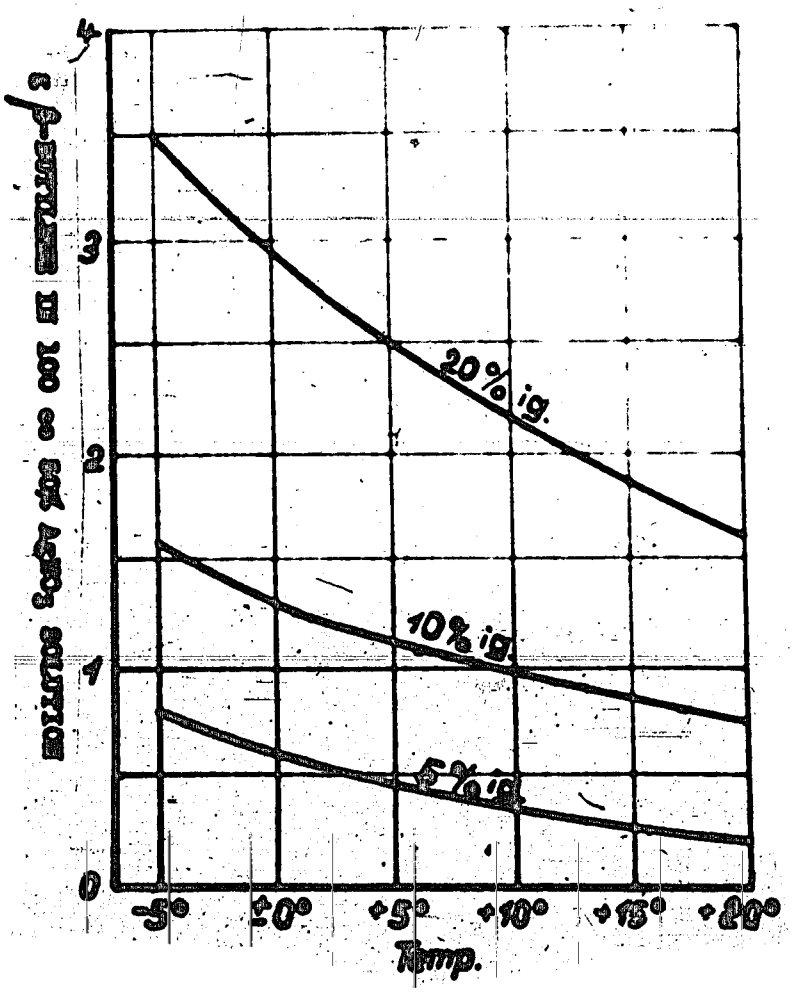
SOLUBILITY OF β-BUTYLENE IN 10% Ag_2SO_3 SOLUTION IN RELATION TO THE TEMPERATURE



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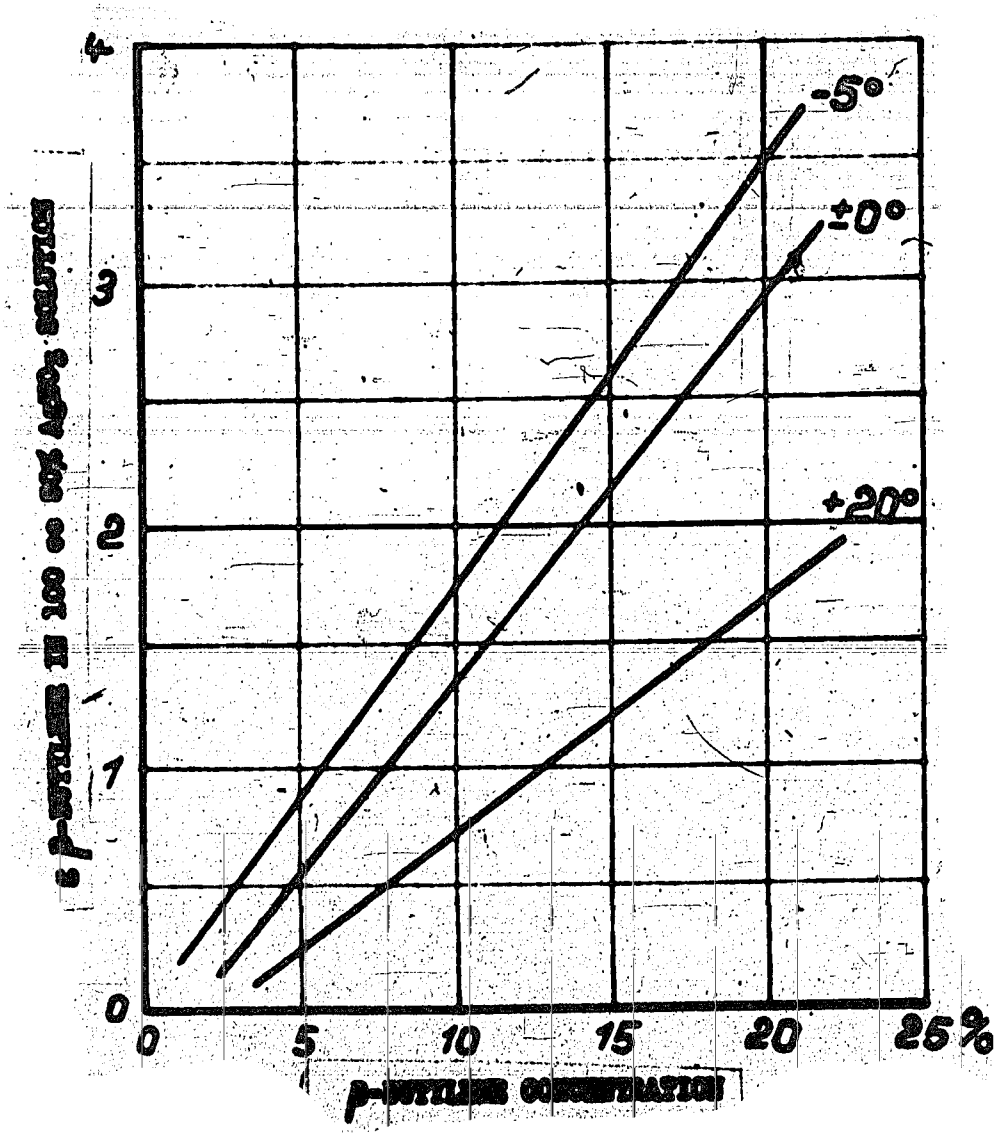
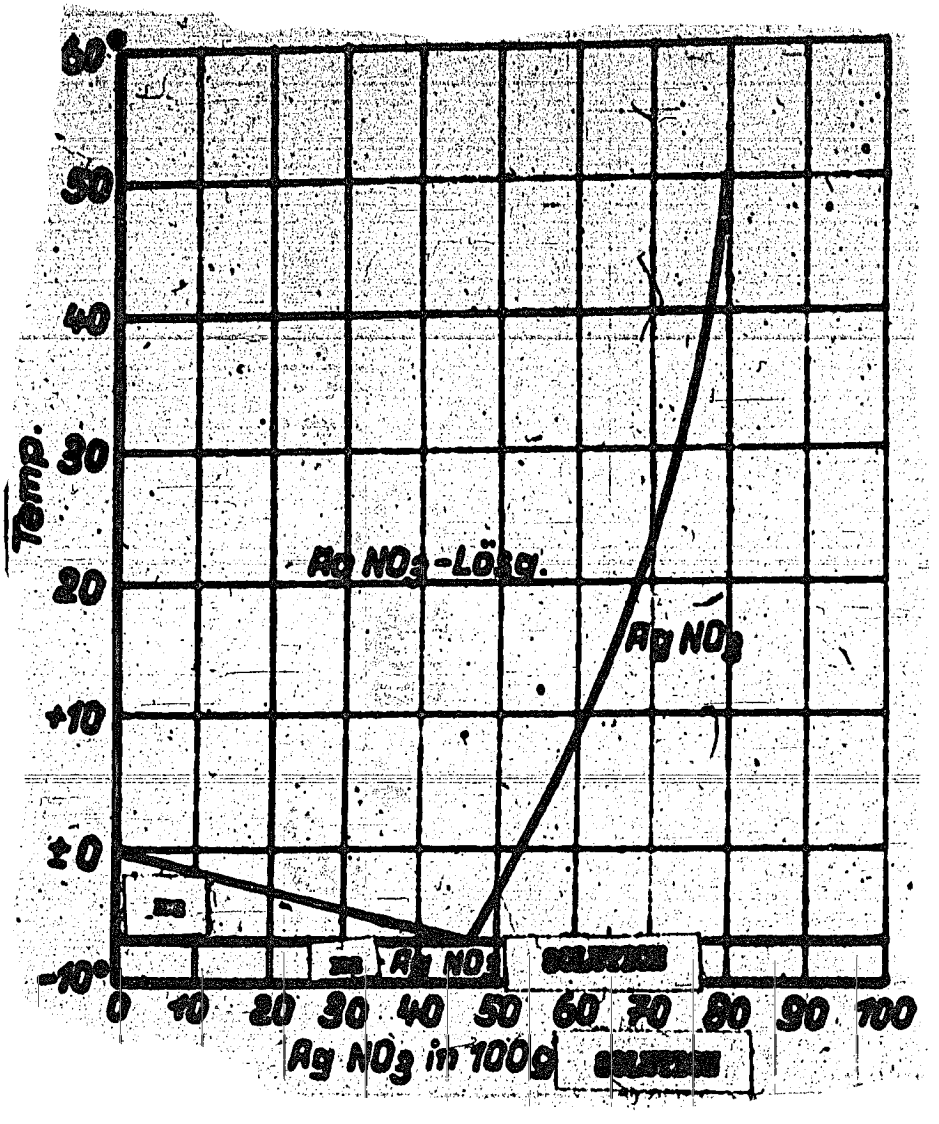
SOLUBILITY OF β-BUTYLEIER IN 80% $AgClO_3$ SOLUTION IN RELATION TO THE BUTYLEIE CONCENTRATI




60
50
40
30
20
+10
±0
-10°
Temp.
Ag NO3-Lösg.
Ag NO3
0 10 20 30 40 50 60 70 80 90 100
Ag NO3 in 100

APPARATUS FOR THE DETERMINATION OF THE BUTYLENE ABSORPTION AND THE RATE OF ABSORPTION OF A 80% $AgNO_3$ SOLUTION

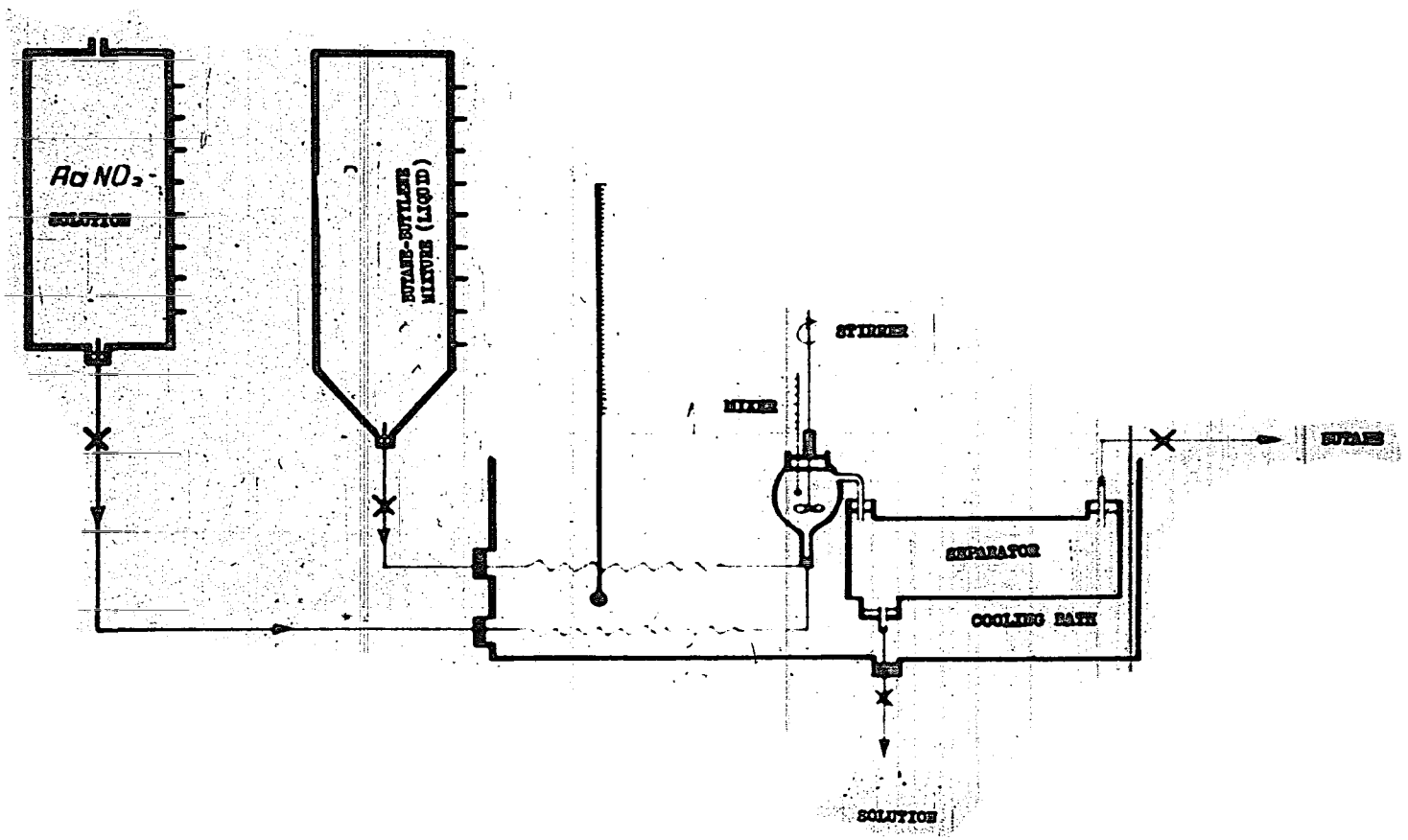


Bild 11

Bild 11

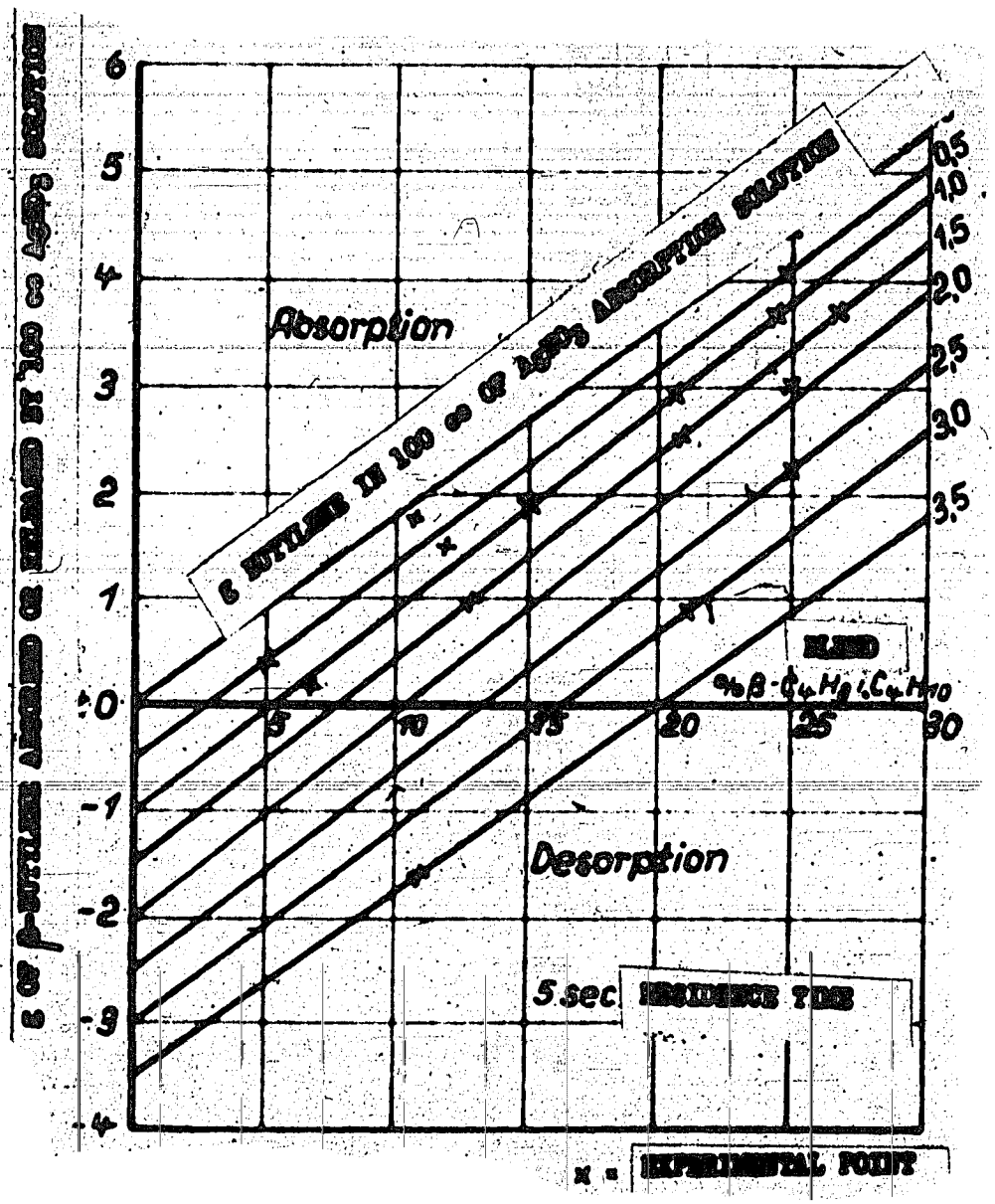


Bild 12

Bild 12

12

RELATION BETWEEN THE PURITY OF BUTYLENE AND SPECIFIC TIME

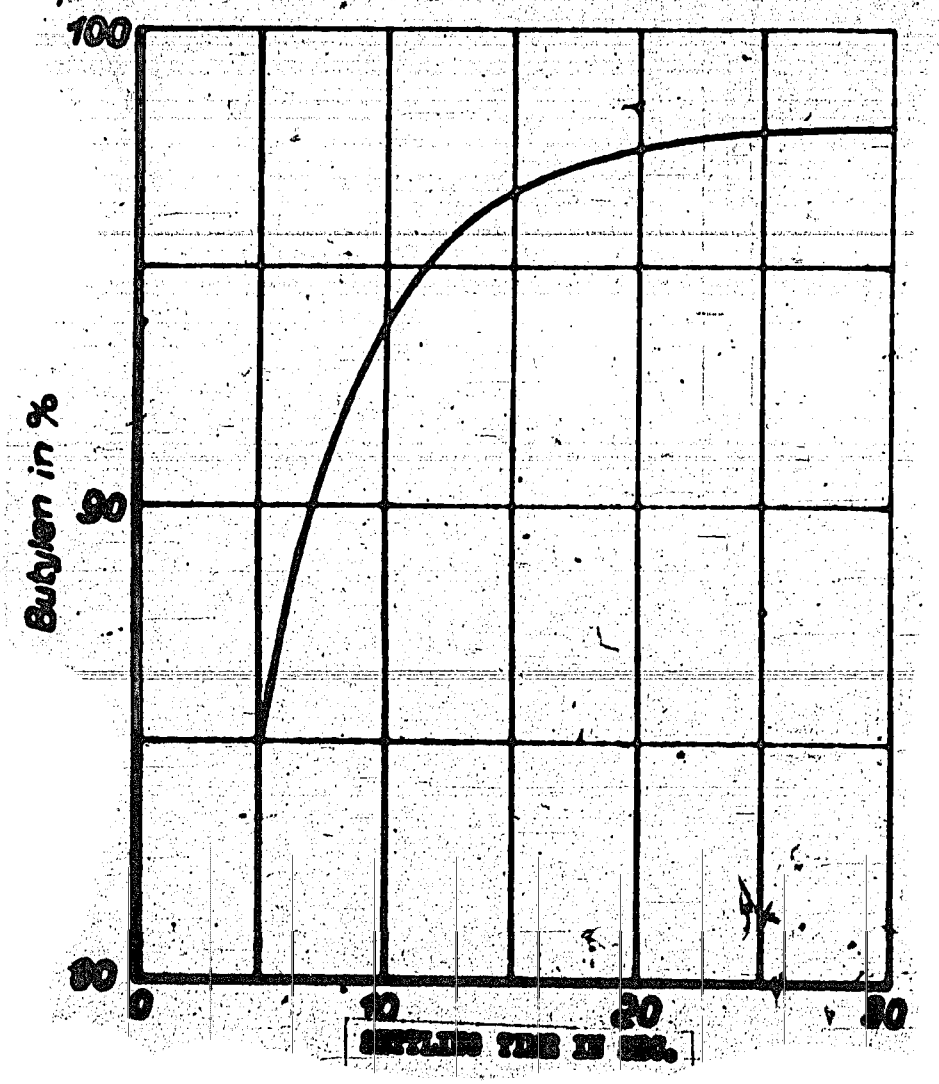


Bild 13

Bild 13

RELATION BETWEEN THE NUMBER OF STAGES AND THE VOLUME RATIO BUTANE-BUTYLENE: $AgNO_3$ SOLUTION

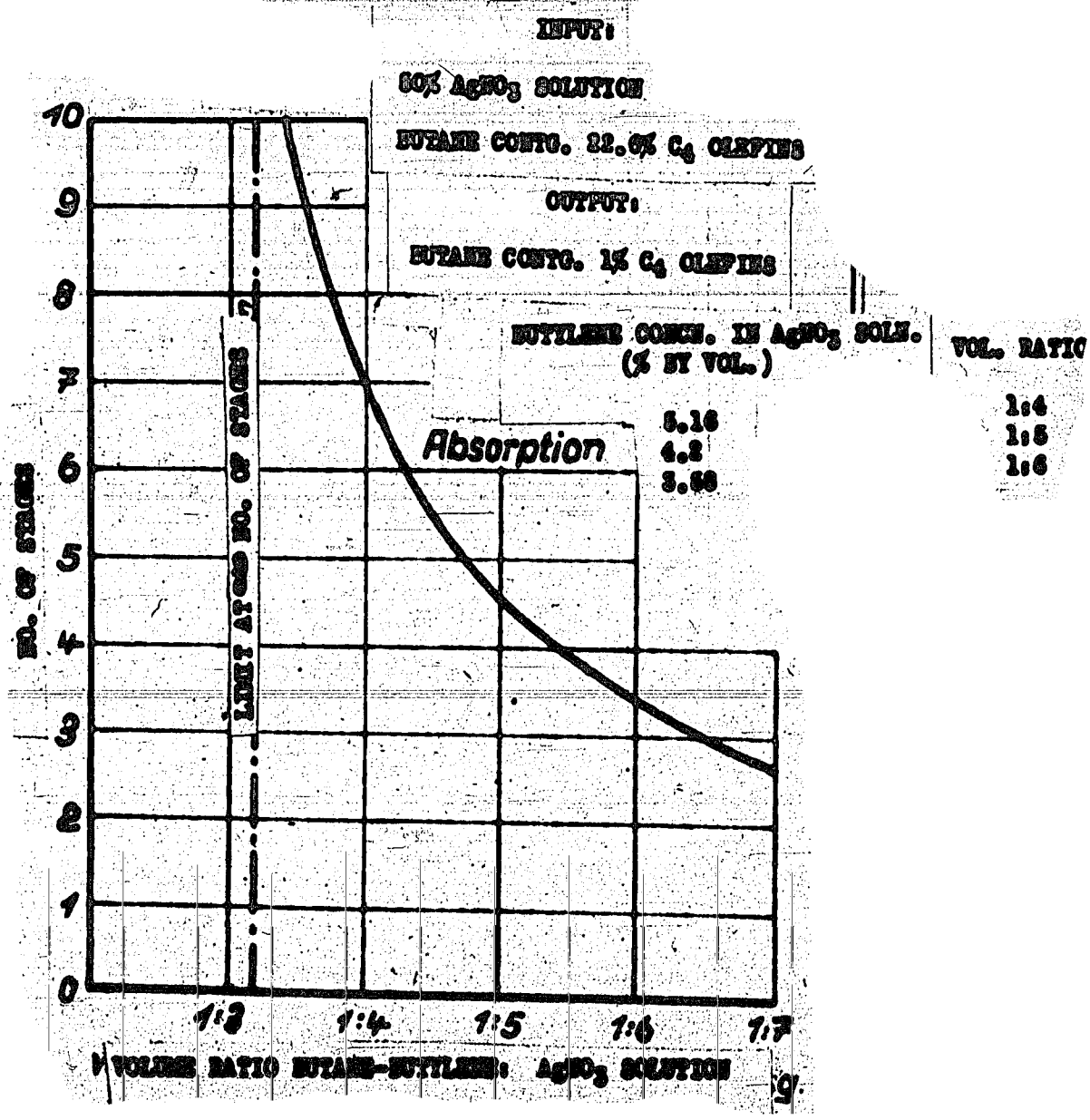


Bild 14

Bild 14

RELATION BETWEEN THE NO. OF STAGES AND THE BUTYLENE CONTENT IN THE OUTGOING BUTANE

INLET:

BUTANE-BUTYLENE: $AgNO_3$ SOLUTION = 1:5 (BY VOL.)

BUTANE CONTG. 22.6% BUTYLENE

OUTPUT:

BUTYLENE CONCN. IN $AgNO_3$ SOLN. (% BY VOL.)

BUTYLENE CONCN. IN OUTGOING BUTANE

1%
2%
3%

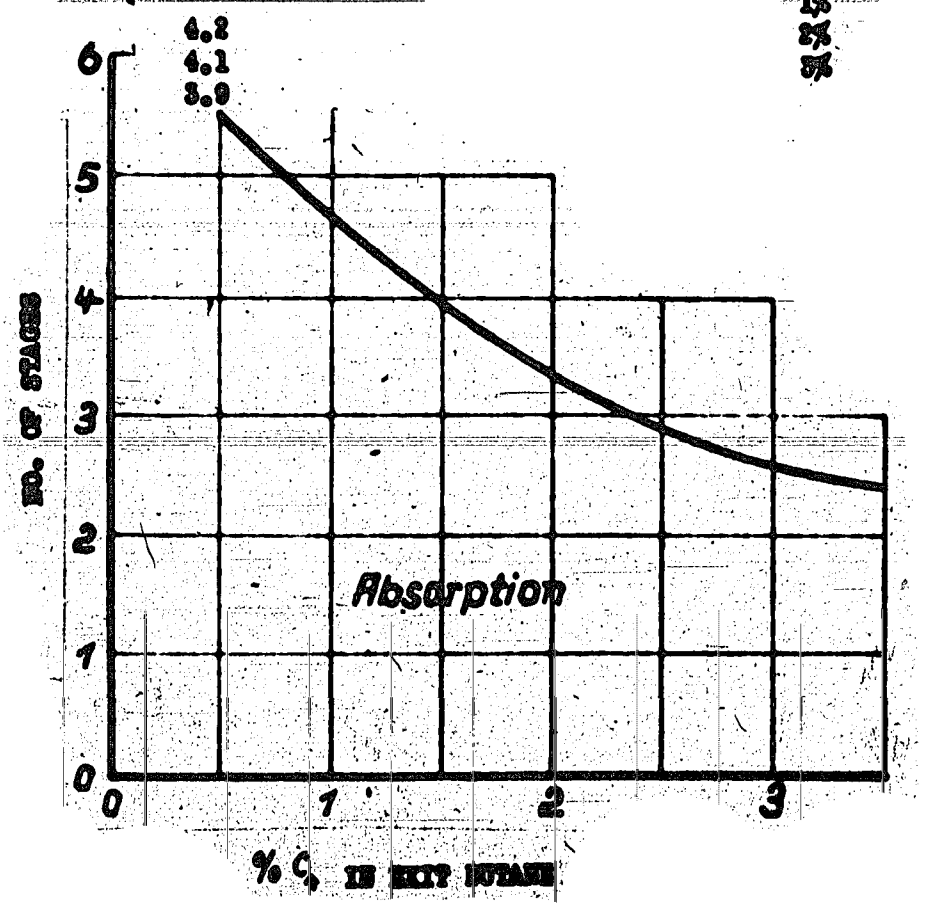


Bild 15

RELATION BETWEEN THE NUMBER OF STAGES AND THE BUTYLENE CONCENTRATION OF THE INCOMING $AgNO_3$ SOLUTION AND THE BUTYLENE CONTENT OF THE OUTGOING BUTANE

INLET:

BUTANE-BUTYLENE: $AgNO_3$ SOLUTION = 1:5 (BY VOL.)

BUTANE CONTG. 22.% BUTYLENE

OUTLET:

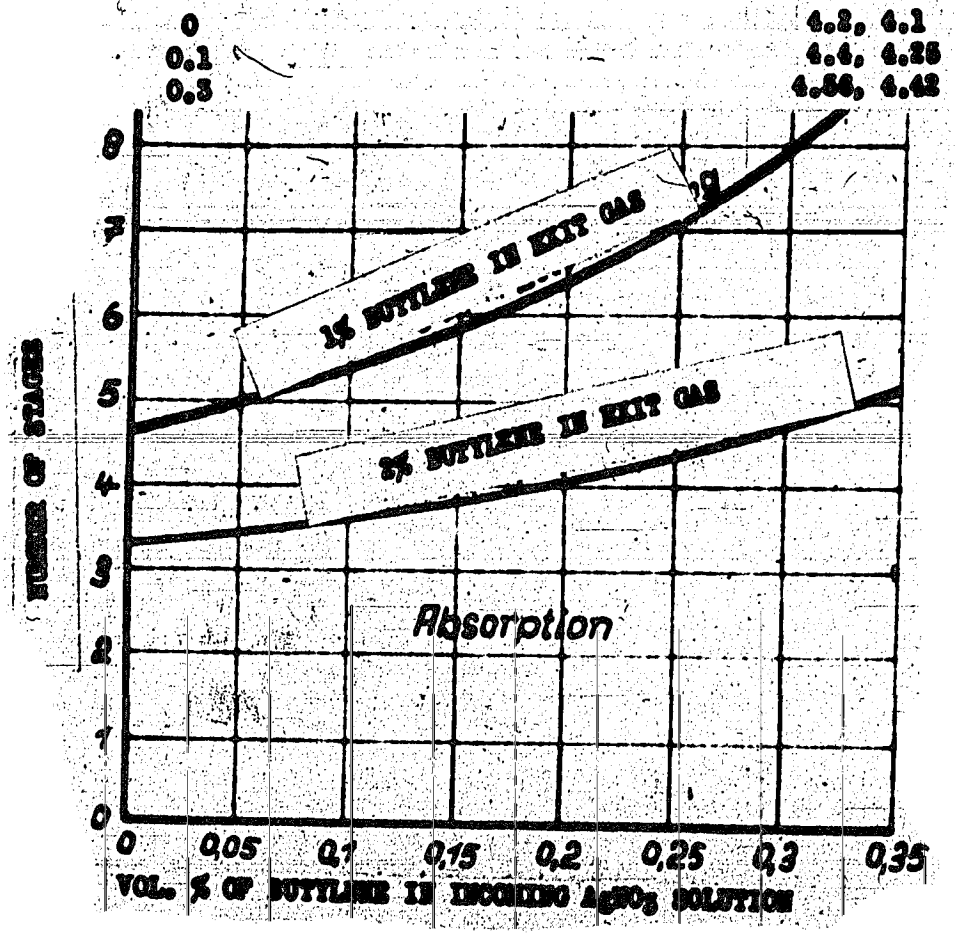
BUTANE CONTG. 1 AND 2% BUTYLENE

CONCN. OF BUTYLENE IN INCOMING $AgNO_3$ SOLN. (% BY VOL.)

0
0.1
0.3

CONCN. OF BUTYLENE IN OUTGOING $AgNO_3$ SOLN. (% BY VOL.)

4.2, 4.1
4.4, 4.25
4.56, 4.42



[illegible] BETWEEN THE NO. OF GRAINS AND THE BUTYLENE CONCENTRATION OF THE IN-COMING BUTANE

INPUT:

BUTANE-BUTYLENE: $AgNO_3$ SOLN. = 1:5 (BY VOL.)

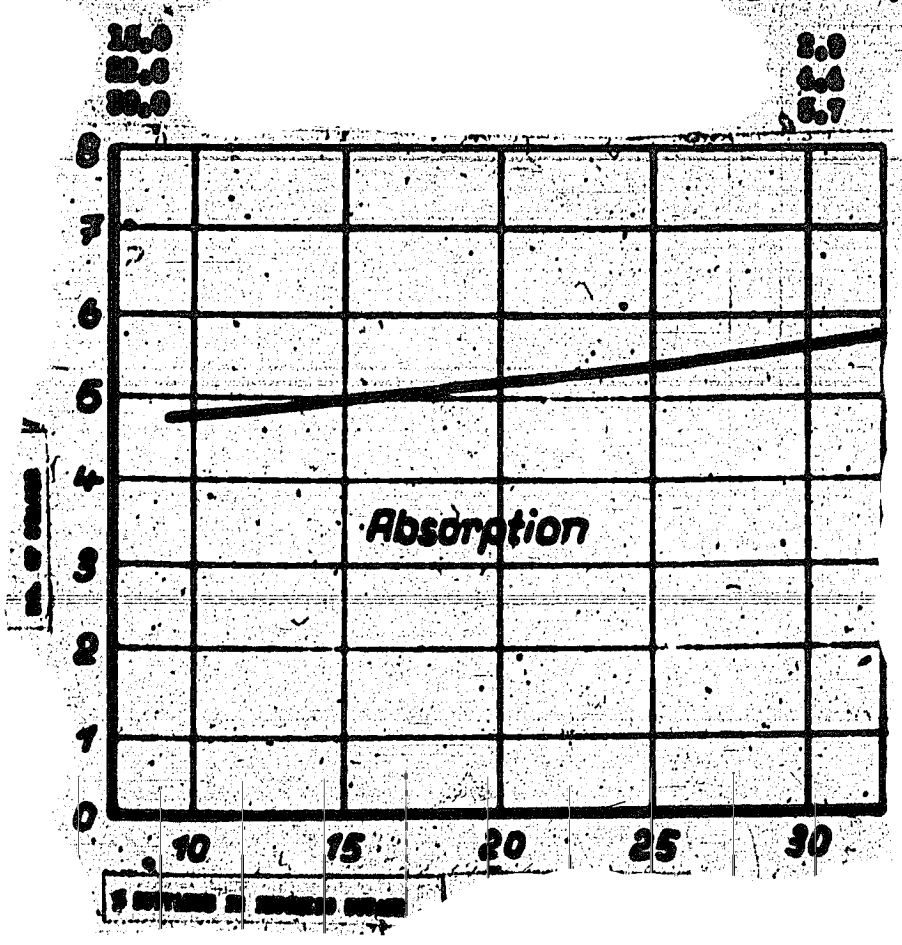
0.25 BY VOL. OF BUTYLENE IN $AgNO_3$ SOLN.

OUTPUT:

% BUTYLENE IN BUTANE

CONC. OF BUTYLENE IN INCOMING BUTANE (% BY VOL.)

CONC. OF BUTYLENE IN OUTGOING $AgNO_3$ SOLN. (% BY VOL.)



% BUTYLENE IN INCOMING BUTANE

RELATION BETWEEN THE NO. OF DESORPTION STAGES AND THE VOLUME RATIO $AgNO_3$ + BUTYLENE:BUTANE

INPUT:

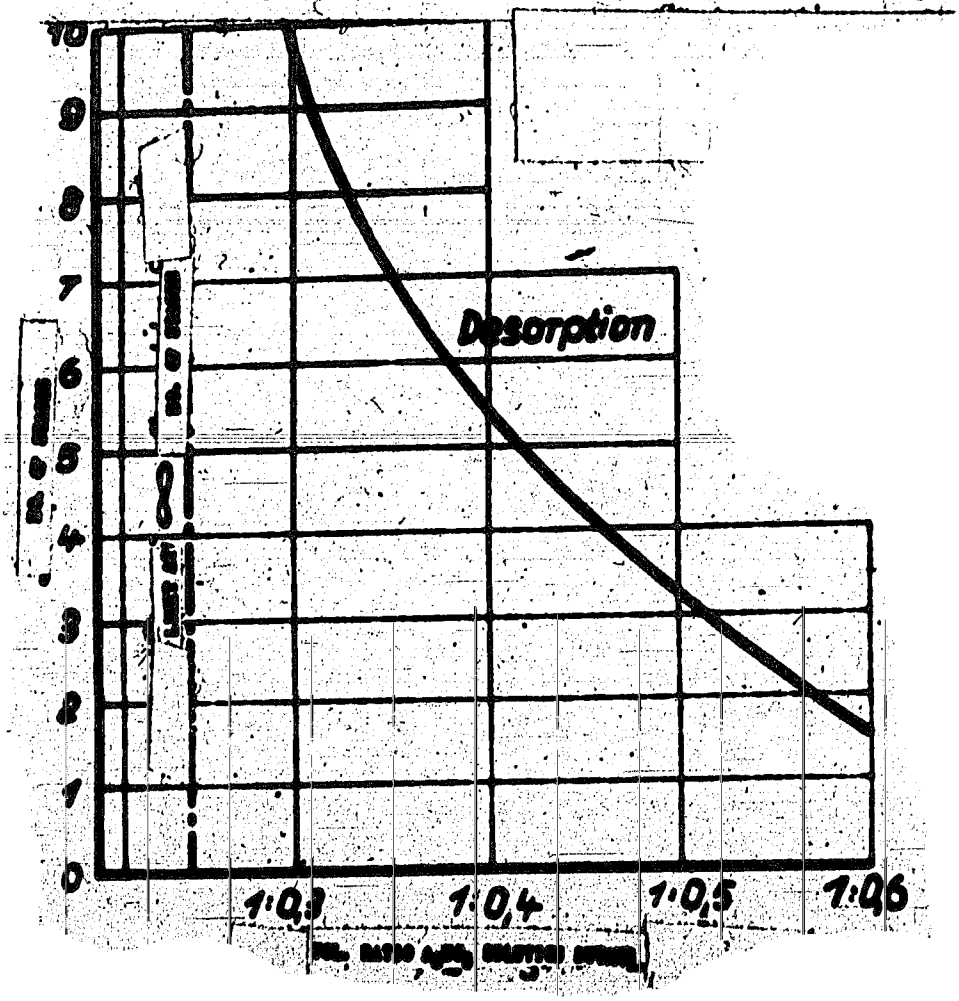
0.3% BUTYLENE IN BUTANE, RATIO OF $AgNO_3$ SOLN.: BUTANE = 5:1

4.45% BY VOL. OF BUTYLENE IN $AgNO_3$ SOLN. (FROM ABSORPTION TOWER BUTANE-WITH 2% BUTYLENE, 0.3% BUTYLENE IN $AgNO_3$ SOLN., 4.7 STAGES)

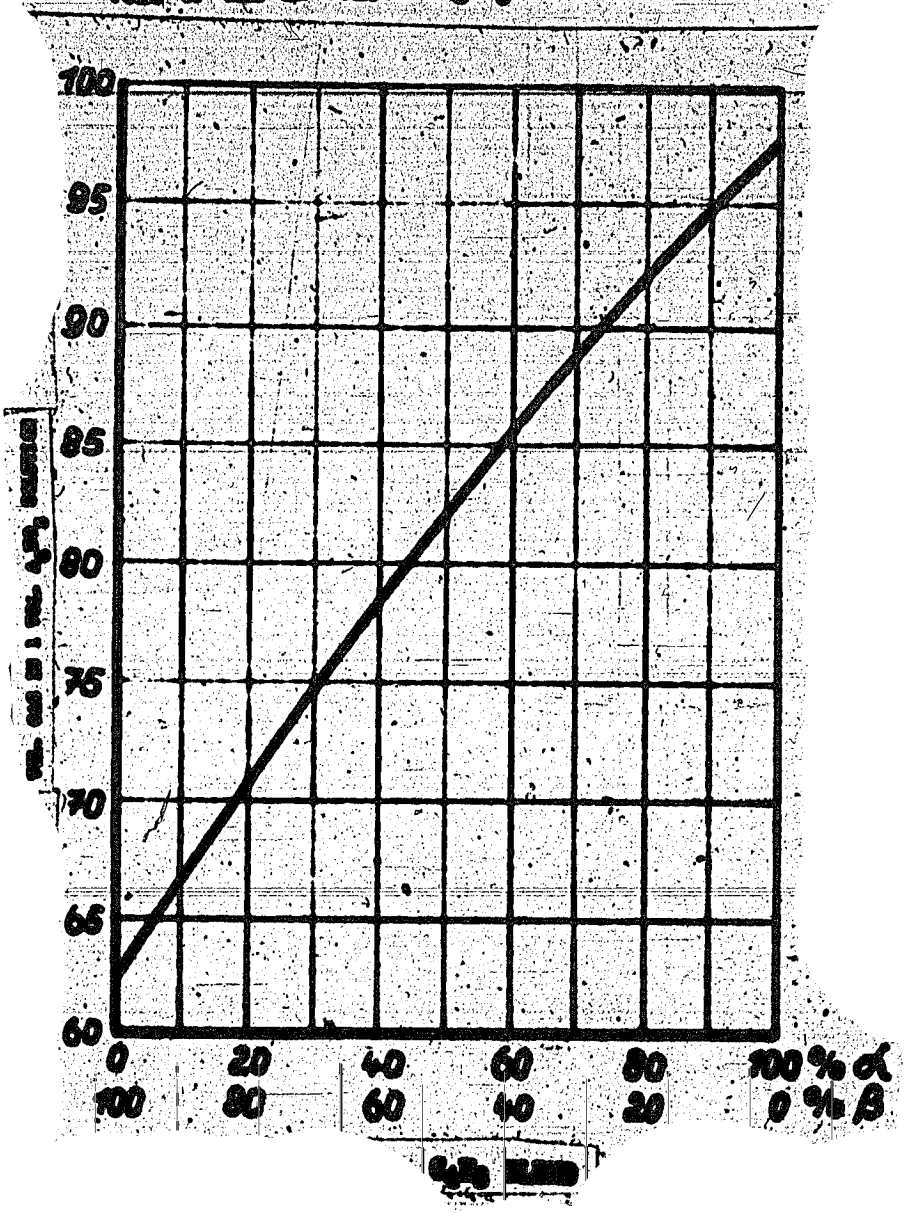
OUTPUT:

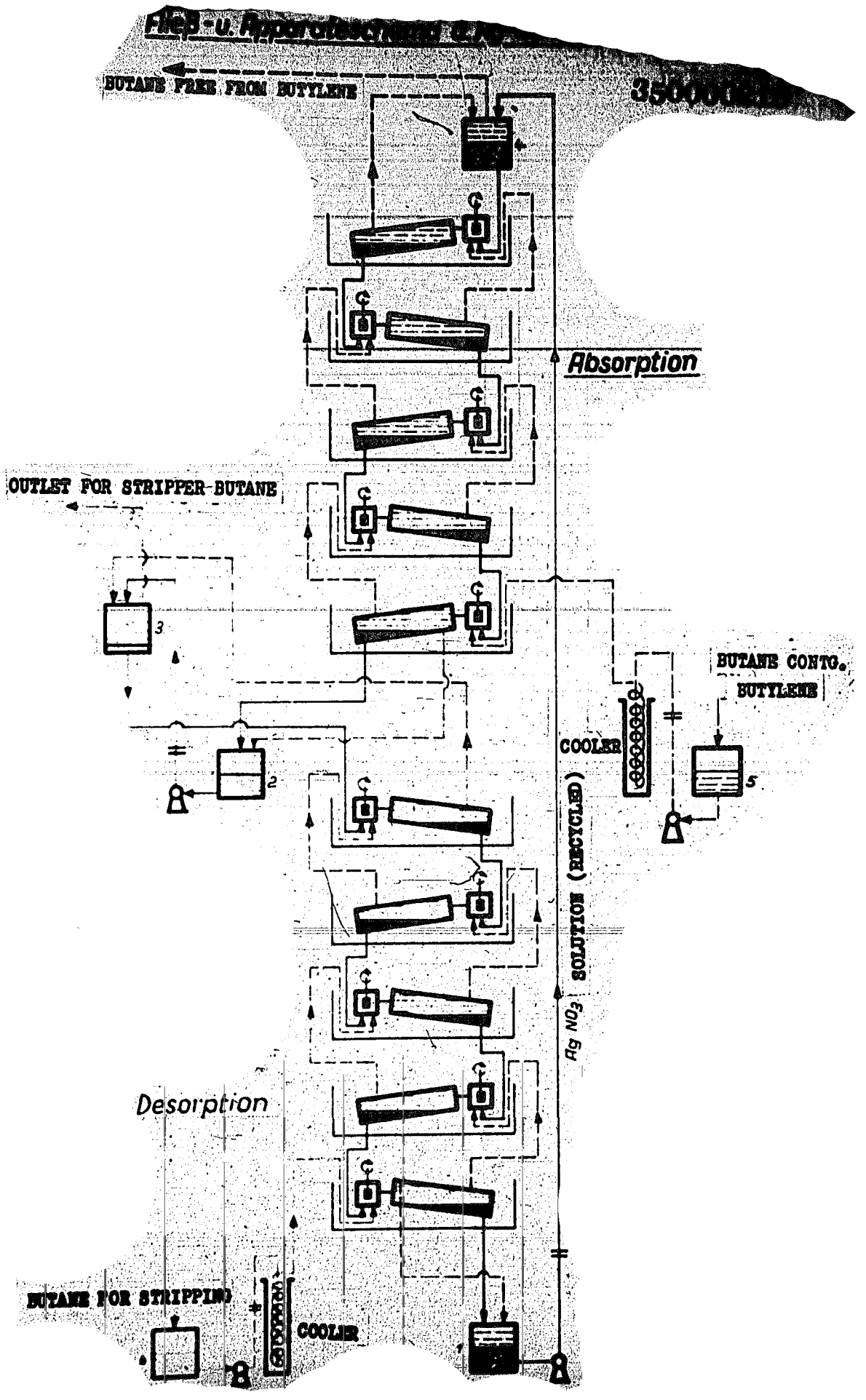
0.3% BY VOL. BUTYLENE IN $AgNO_3$ SOLN.

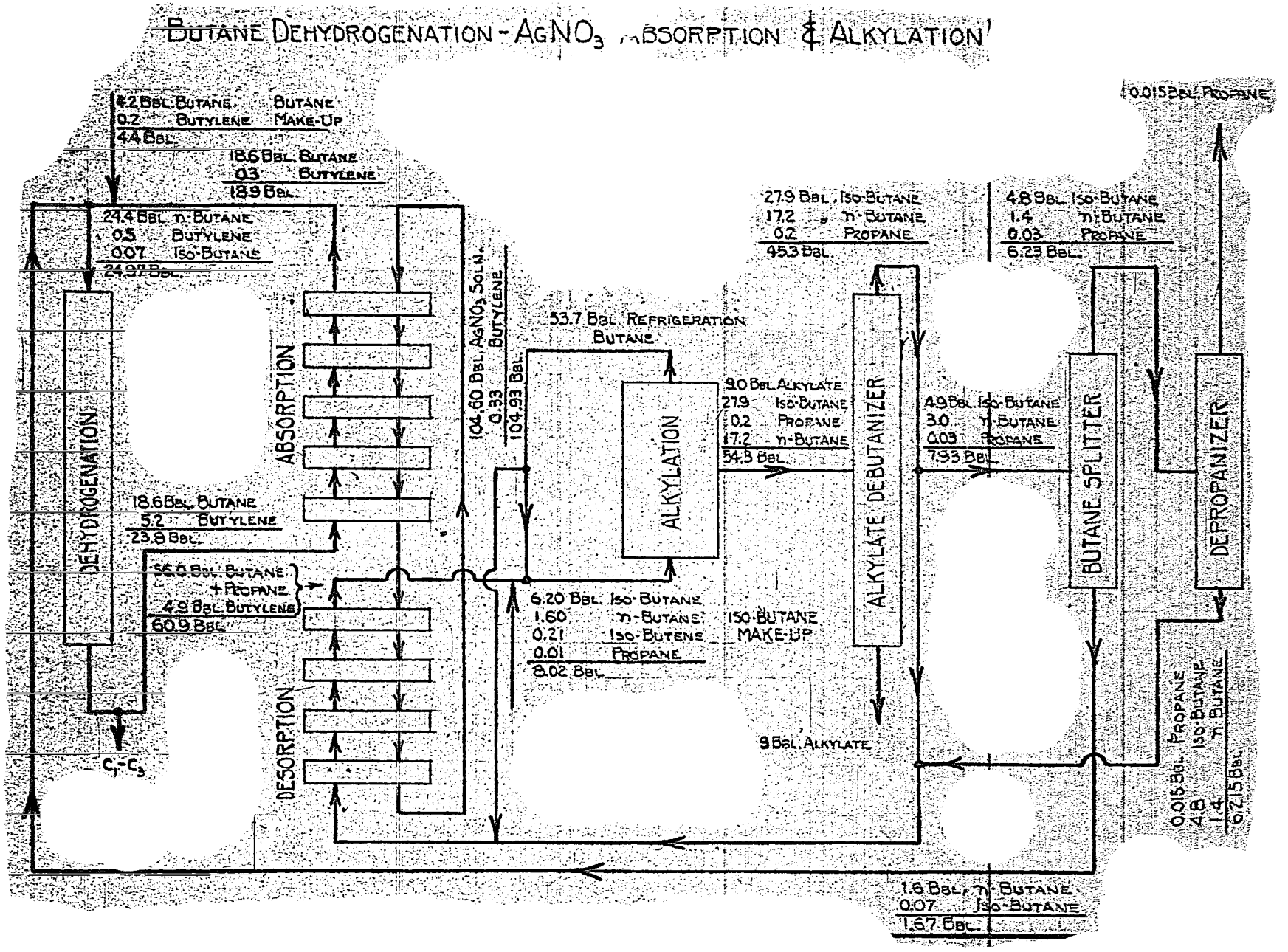
CONCN. OF BUTYLENE IN OUTGOING BUTANE (% BY VOL.)	VOL. RATIO
23.84	1:0.3
10.2	1:0.4
0.2	1:0.5



SOLUBILITY OF C_6- AND β-BUTYLENE BLENDS IN 60% $AgNO_3$ SOLUTION AT 30-37°.




BUTANE FREE FROM BUTYLENE
Absorption
OUTLET FOR STRIPPER-BUTANE
3
2
BUTANE CONTG.
BUTYLENE
COOLER
5
Ag NO3 SOLUTION (RECYCLED)
Desorption
BUTANE FOR STRIPPING
COOLER
1


BUTANE DEHYDROGENATION - AgNO3 ABSORPTION & ALKYLATION
4.2 Bbl. Butane
0.2 Butylene
4.4 Bbl.
Butane Make-Up
18.6 Bbl. Butane
0.3 Butylene
18.9 Bbl.
24.4 Bbl. n-Butane
0.5 Butylene
0.07 Iso-Butane
24.97 Bbl.
DEHYDROGENATION
ABSORPTION
DESORPTION
104.60 Bbl. AgNO3 Soln.
0.33 Butylene
104.93 Bbl.
53.7 Bbl. Refrigeration Butane
ALKYLATION
9.0 Bbl. Alkylate
27.9 Iso-Butane
0.2 Propane
17.2 n-Butane
54.3 Bbl.
27.9 Bbl. Iso-Butane
17.2 n-Butane
0.2 Propane
45.3 Bbl.
ALKYLATE DEBUTANIZER
4.8 Bbl. Iso-Butane
1.4 n-Butane
0.03 Propane
6.23 Bbl.
0.015 Bbl. Propane
4.9 Bbl. Iso-Butane
3.0 n-Butane
0.03 Propane
7.93 Bbl.
BUTANE SPLITTER
DEPROPANIZER
18.6 Bbl. Butane
5.2 Butylene
23.8 Bbl.
56.0 Bbl. Butane + Propane
4.9 Bbl. Butylene
60.9 Bbl.
C1-C3
6.20 Bbl. Iso-Butane
1.60 n-Butane
0.21 Iso-Butene
0.01 Propane
8.02 Bbl.
150-Butane Make-Up
9 Bbl. Alkylate
0.015 Bbl. Propane
4.8 Iso-Butane
1.4 n-Butane
6.215 Bbl.
1.6 Bbl. n-Butane
0.07 Iso-Butane
1.67 Bbl.