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The Preparation and Properties of Diethylene Glycol Dinitrate

PART IV

The Continuous Process for DEGN Manufacture

S. E. Smith

INCLOSURE 2 TO REPORT No. R-1814-50

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THE PREPARATION AND PROPERTIES OF DIETHYLENE
GLYCOL DINITRATE

Parts I and II. E.R.D.E. Report No. 18/R/48 - Ref. C.R.Temp. 7/11/2/1

By

S. Masterman
S.E.Smith
W.E.Turner

Parts III.	E.R.D.E. Report	2/R/49	-	Ref. X.R. 510/1.
" IV.	" "	3/R/49	-	" X.R. 510/2
" V.	" "	4/R/49	-	" X.R. 510/3
" VI.	" "	21/R/49	-	" X.R. 510/5

by

S.E.Smith

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SUMMARY

I. Objects of the investigation

To examine the properties of diethylene glycol dinitrate, and to develop a method for its manufacture from diethylene glycol.

II. Scope of the investigation

The requirements of commercial diethylene glycol for nitration to the dinitrate for Service use have been investigated. The optimum conditions for the nitration, and for the stabilisation of diethylene glycol dinitrate, have been determined by laboratory and semi-technical scale investigations, and batch and continuous pilot plants for these operations have been developed.

The manufacture of D.E.G.N. and recovery of the spent acid have been established on the semi-manufacturing scale and quantities of the product supplied for experimental propellant manufacture.

The chemistry of D.E.G.N., the mechanism of its nitration and the reactions of the spent acid have been given some fundamental study.

No difficulty has been met in obtaining D.E.G.N. of acceptable purity and chemical stability by these processes.

The maximum overall manufacturing yield of D.E.G.N. so far obtained is 90 per cent theory as against 94 per cent for nitroglycerine. This is a disadvantage of D.E.G.N.

The spent acid from D.E.G.N. nitration retains some D.E.G.N. in solution and fumes off at ordinary temperatures after a 'life' depending on the composition of the acid. An acid composition for continuous nitration has been devised to give a spent acid with a safe life around 12 hours at 20°C. A procedure has been developed in which the spent acid from the continuous process is run directly down a dinitration tower in which the dissolved organic matter is destroyed. This involves the recovery of NO₂ as 60 per cent nitric acid and some additional nitric acid concentration.

The physical, chemical, explosive and physiological properties of diethylene glycol dinitrate so obtained have been determined.

Conclusions

1. D.E.G.N. can be safely manufactured in the same types of plant, batch or continuous, as are used for nitroglycerine. The continuous process is more suitable for operation with a continuous waste acid denitration. In both batch and continuous nitration the safety of D.E.G.N. enables simplifications to be made. The yield of D.E.G.N. is less and the consumption of nitric acid is somewhat higher than for nitroglycerine.
2. The spent acid from D.E.G.N. nitration is unstable and needs to be decomposed directly and continuously. Denitration tower practice has been found suitable for this purpose and can be safely linked up with continuous nitration.
3. D.E.G.N. is superior to nitroglycerine in safety in handling.
4. D.E.G.N. appears to have no disadvantageous physiological effects during the short manufacture to date; the long term effect on health of the workers is yet to be determined.

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E.R.D.E. REPORT NO. 3/R/49.

The Preparation and Properties of Diethylene
Glycol Dinitrate.

PART IV.

The Continuous Process for DEGN Manufacture

by

S.E. Smith.

This report does not contain information of overseas
origin.

Submitted by:

A. Foster
S.E.I.

Approved by:

C.H. Johnson
A/C.S., E.R.D.E.

Waltham Abbey,
Essex.

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The manufacture of DEGN and recovery of the spent acid have been established on the semi-manufacturing scale and quantities of the product supplied for experimental propellant manufacture.

The chemistry of DEGN, the mechanism of its nitration and the reactions of the spent acid have been given some fundamental study.

No difficulty has been met in obtaining DEGN of acceptable purity and chemical stability by these processes.

The maximum overall manufacturing yield of DEGN so far obtained is 90 per cent theory as against 94 per cent for nitroglycerine. This is a disadvantage of DEGN.

The spent acid from DEGN nitration retains some DEGN in solution and fumes off at ordinary temperatures after a 'life' depending on the composition of the acid. An acid composition for continuous nitration has been devised to give a spent acid with a safe life around 12 hours at 20°C. A procedure has been developed in which the spent acid from the continuous process is run directly down a dinitration tower in which the dissolved organic matter is destroyed. This involves the recovery of NO₂ as 60 per cent nitric acid and some additional nitric acid concentration.

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1. DEGN can be safely manufactured in the same types of plant, batch or continuous, as are used for nitroglycerine. The continuous process is more suitable for operation with a continuous waste acid denitration. In both batch and continuous nitration the safety of DEGN enables simplifications to be made. The yield of DEGN is less and the consumption of nitric acid is somewhat higher than for nitroglycerine.

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/safely

safely linked up with continuous nitration.

3. DEGN is superior to nitroglycerine in safety in handling.

4. DEGN appears to have no disadvantageous physiological effects during the short manufacture to date; the long term effect on health of the workers is yet to be determined.

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Reference X.R.510/2.

I. Introduction.

In this section of the report a pilot plant for the manufacture of DEGN by the Schmid continuous process is described.

The Schmid plant has been used for many years for the production of nitroglycerine and consists essentially of a colandria type nitrator and an inclined box which functions as a separator. The glycerol and mixed acid are fed continuously to the nitrator and the reaction mixture is cooled by passage through a large number of vertical tubes encased in a brine drum. The emulsion formed overflows into the separator where a constant level of separation is maintained by continuously taking off the product from the top, and spent acid from the bottom of the vessel. The crude product is deacidified and stabilised in a series of glass washing columns, which also operate continuously.

A continuous process is especially suitable for the manufacture of DEGN because of the opportunity it affords of disposing of the unstable waste acid (see Part II), within a reasonable period of time. Continuous counter-current washing is advantageous for working up the prewash liquors of recoverable strength.

The nitrator and separator of the DEGN Schmid pilot plant were designed by scaling down the 600 Kgm/hr. nitroglycerine plant to approximately 1/10th full size, i.e. so as to produce 100 lb./hr. of DEGN.

The washing plant was made from standard pyrex glass pipe and fittings.

It has been shown that DEGN can be safely and conveniently made continuously by this system. Overall yields of 88% of theoretical have been obtained on runs of short duration: this should increase to 90% with longer periods of nitration.

Methods for the continuous recovery of the spent acid and prewash liquors produced have been worked out and are discussed in Part V. of the report.

/II. Description

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II. Description of Plant.

The nitration and washing plant is housed in the former N.G. No.2 Washing House at Waltham. The Schmid House is thus at a lower level than the Batch Nitrating Hill, being on the same level as the No.1 Washing House, which is now used for batch washing of DEGN.

The other buildings on the site such as the Solution House, Charge House, Wash Water Settling House, etc., serve for both the batch and continuous plants, and are as described in Part III; the supplies and services available to the two plants are, in most respects, identical. Additional piping was installed between the Charge House and the Schmid House to carry brine and mixed acid supplies; and return piping for brine and waste acid was also laid.

In the case of the N.G. Schmid plants, glycerol and mixed acid for nitration are delivered to the Nitrating House from pressurised vessels in the Charge House, but owing to the distance between the two houses a different arrangement was made for the DEGN plant. The acid runs from the Charge House by gravity flow to the nitrator, and the DEG is delivered from pressurised vessels situated inside the Nitrating House.

DEGN from the Schmid House is transported to the Washing House as an emulsion which is first elevated into a high level pipe and then discharged from this into the original gutter connecting the Batch Nitrating Hill with the Washing House.

Drawings of all the items of plant are not available, but three drawings are reproduced which show the details of the nitrator and separator. In addition, six photographs showing several sections of the plant as installed, and a flow sheet and a flow diagram of the process, are reproduced.

Supply and Handling of Raw Materials.

DEG: (Specification see Part II). This is supplied in 40 gal. drums and is blown through a 1" m.s. line into either of the DEG service tanks by opening the appropriate cock.

Mixed Acid: This is mixed from 98-99% Nitric Acid and 20% Oleum, at the Acid House and stored in a 1,000 gal. stainless steel tank. It is pumped to the Charge House above the Batch Nitrating Hill where it is received in a 180 gal. m.s. tank. From this it is filtered by pumping through a stainless steel meta filter, into either of two 50 gal. s.s. service tanks. The outlets from these tanks are connected by a s.s. line direct to the rotameter in the Schmid House in the feed to the nitrator.

Displacement Acid: This acid, which is used at the beginning and the end of each run, is mixed at the Acid House from recovered nitric acid and sulphuric acids, in a small mixing plant, and sufficient for each run is trucked to the Egg House below the Nitrating Hill. Here it is blown from a 30 gal. s.s. egg, through a s.s. line, to the Displacement Acid Tank at the Schmid House.

Process Water: River water is pumped to a water tower and piped by gravity to the Schmid House where it is filtered through a leaf filter before use.

/Soda

Soda Solution and Softened Water; are prepared at the Solution House, elevated by compressed air eggs to the Charge House, and stored in galvanised tanks. Supplies are piped to the Schmid House by gravity flow.

Other Services:

Warm Water Supply: This is used at the Schmid House to control the temperature of the DEG supply. It is obtained by passing steam into cold river water, in a jacketed 145 gal. steel tank, on the mound outside the house. The supply is drawn off from the top of the tank which is kept full by a ball valve on the cold water inlet; the temperature is maintained at 30°C. by a thermostat valve on the steam line.

Compressed air: This is delivered to the Schmid House at 80 lb./sq. in.

The cooling brine used for nitration is 30-35% Calcium Nitrate containing 7 $\frac{1}{2}$ % Sodium Nitrate, which is circulated to the Schmid House at a temperature of -10°C., from the high level store tank (2,560 gals) above the Batch Nitrating Hill. It is returned to an ammonia refrigerator and pumped from there back to the high level tank.

The Charge House is a two-roomed building and was described in part III; it accommodates on one side the high level acid storage and supply tanks, and on the other the wash solution supply tanks.

Schmid Nitrating House.

This is a circular wooden building, 20 ft. diameter, traversed and mounded over on all sides to a height of 20-30 ft. with a tunnel entrance. A platform on one side of the house, originally supported three N.G. Washing tanks, which have now been removed. Steel joist pillars, tied together by cross-members which pass through the wall of the building into the concrete traverse, were erected across the building in front of the washing platform, and support the principle items of the Schmid plant. A wooden platform on two levels, is built out from the front of the steelwork and provides working space from which the nitrator and separator are controlled. Access to this platform from floor level is by a stairway on the same side of the house as the tunnel entrance; an escape door at the far end of the platform leads to the top of the mound. The floor and platforms are covered with sheet lead. The building has a number of small windows around the wall just below the eaves, and is also illuminated by electric bulbs in flame-proof fittings.

The nitrator and stirrer motor are mounted together on a back-plate which is bolted in an upright position to the steel joists about halfway across the house. The separator is supported at a lower level to one side of the nitrator, on a steel box framework, built out from the main girders.

The main nitration platform level is 7'6", the smaller platform under the separator being 6'0" above floor level. On the far side of the nitrator is the motor control gear, Area air valve, and a control panel. Under the nitrator platform are the DEG service tanks and the drowning tank. Two light steel frames which stand on the floor, on the entrance side of the house, support the prewash and final washing columns, their heights being

/such

such that DEGN flows from the separator to the prewash unit, and thence to the final wash unit by gravity.

On the original washing platform, which is also reached by a wooden stairway, are two small hand washing tanks; a filter for process water stands on the floor underneath the platform. Two lead labyrinths, one on floor level and the other at the side of the washing platform, complete the main plant items in the house. Wash waters containing DEGN are passed to the Wash Water Settling House, down a lead gutter, and uncontaminated waste water is taken away by a covered channel in the floor.

On the roof, outside the house, is a Displacement Acid Tank and in the traverse are air lifts for waste acid and prewash liquor.

Control of Supplies.

DEG; The high pressure air supply is reduced to 27 lb./sq.in. by an Arca reducing valve and regulator, accessible from the nitration platform, and the controlled low pressure applied to the DEG supply tanks, which are duplicated so that one can be recharged while the other is on feed. The air to each tank is controlled by a globe valve on the control panel, and the pressure on each tank, as well as at the Arca, is shown by gauges on the panel. The tanks are connected in parallel and have identical fittings, viz: inlet controlled by brass plug cock, dip-pipe outlet, air connection, drain cock, thermometer socket, safety valve, pressure tapping and air release cock. No liquid level indicators are fitted but the DEG used is metered and the tanks can be dipped when not on service. The capacity of the tanks is 40 gals. and 100 gals.

To change from one to the other during a run, while the first tank is still delivering DEG, the second tank is put under pressure and the outlet cock opened, and then the first tank can be shut off, the pressure released, and the tank refilled. The outlet lines from the tanks are fitted with strainers to prevent solid particles from reaching the rotameter and injector.

It was found necessary to regulate the temperature fairly closely in order to meter the DEG with sufficient accuracy by rotameter. The tanks are fitted with coils for circulating water to regulate the DEG temperature, but this system was discontinued. The DEG is now passed through a tempering coil in the delivery line from the tanks to the rotameter; the coil is immersed in a small tank through which warm water is kept flowing, at a rate controlled from a valve on the control panel. In passing through the coil the DEG attains a steady temperature.

The rotameter is a free float type, range 0.01 - 0.20 gals./minute DEG with m.s. fittings, and is controlled by a needle valve. A mercury-in-glass thermometer, by which the DEG temperature is observed, is inserted in a pocket on the line between the rotameter and the injector. Immediately before the injector is a branch pipe normally closed by a cock; this is used to return the DEG to the tank not on feed at the beginning of a run, until the DEG has reached the operating temperature which is $20^{\circ}\text{C.} \pm 0.1^{\circ}\text{C.}$

The injector is attached by a bracket to the nitrator stirrer casing, in an off-central position above the centre tube of the nitrator; it is an original glycerine injector from the N.G.

/Schmid

Schmid plant. It has a spring loaded plunger operated by a projecting lever, by which the DEG can be quickly shut off by hand; the sleeve which on the original plant automatically locked the injector shut under certain abnormal conditions of the plant, has been removed, and the jet has been reduced in size to 1/16".

Mixed Acid enters the nitrator at the bottom of the drowning tube from a rotameter of the free-float type.

The bottom of the rotameter is connected directly to the mixed acid line from the Charge House.

The temperature of the mixed acid is not controlled.

Displacement Acid may also be fed to the bottom of the nitrator through the same rotameter, by gravity from the D/A tank, which is mounted on the outside roof of the house. This is a 35 gal. stainless steel horizontal tank, its fittings comprising a flanged inlet at the top, outlet at one end, a thermometer socket, air spray coil, water cooling coil, and gauge glass with drain cocks.

Both acid supplies are controlled by s.s. plug cocks operated from the nitrator platform; one of the main valves is first opened fully and the flow is then regulated by a s.s. plug cock under the rotameter.

Cooling brine to the nitrator is controlled by gate valves on both inlet and outlet. The inlet and outlet temperatures are shown by Negretti & Zambra mercury-in-steel dial thermometers on the control panel.

Nitrator.

The nitrator consists essentially of a s.s. calandria, 10 $\frac{1}{4}$ " int. diam. x 1'11 $\frac{3}{4}$ " outside tube plates, with a central tube 4" diam. and 30 tubes each 13/16" int. diam., 1" ext. diam. x 1'11 $\frac{3}{4}$ " long, arranged in two concentric circles of twelve and eighteen.

The central tube is welded into the header plates; the tubes which are cold drawn s.s. carefully annealed and polished internally, are swelled to 1.1/32" outside diameter for 1.1/2" at each end, and expanded into the header plates. The lips at the top and bottom of the central tube are rounded off to assist circulation.

The drum has a brine inlet on one side near the bottom, and outlet on the opposite side near the top. A brine drain cock is provided at the bottom, and an air release cock at the top of the drum.

Baffles of 1/8" m.s. cut away on one side, with 1.1/16" diam. holes for the tubes to pass through are spaced at intervals within the drum: these are placed with the cut-away edges alternately opposite the brine inlet and outlet, to ensure thorough circulation of the brine.

At the lower end of the calandria is a dished bottom, bolted on and sealed by a lead ring. A raised serrated ridge on the upper surface clamps down on to the lead (chemically pure lead), which is melted into a groove on the lower surface.

/The

The bottom has a flanged outlet to which the drowning tube is attached. This is 2'9" long and extends downwards through the nitration platform to reach the drowning tank.

The drowning flap is a hinged plate attached to a flange at the lower end of the drowning pipe. The seal is made with a lead washer, and the flap is held in place by a quick-release lever. When operated, this releases the flap and also forces it off the seal, thus ensuring that it opens. There are two flanged side connections at the bottom of the drowning tube above the flap, one for entry of mixed acid and the other, normally closed by a plug cock, for running out the contents of the nitrator after a normal shut-down.

The upper end of the calandria is fitted with a s.s. section similarly bolted on and sealed, and covered by a toughened plate glass window in two sections, through holes in which pass the stirrer, a mercury in glass thermometer, and the DEG feed.

The DEGN and acid emulsion overflow by a tube in the side of the top section into a tundish attached to it; a fume outlet is also fitted to this section.

The sides of the calandria drum are lagged to a depth of 2½" with loosely crumpled aluminium foil, retained in place by an outer steel casing.

The brine drum is tested to 160 lb./sq.in. hydraulic pressure and to 80 lb./sq.in. with air, with soap suds painted on all joints and expanded ends of tubes; its working pressure is 35 lb./sq.in.

A s.s. stirrer shaft passes down the centre tube, and carries a three bladed propeller, which operates in the bottom of the nitrator, circulating the mixture down the centre tube and up the outer tubes. It originally also had two straight blades near the top of the centre tube, but these were cut off and in addition an inverted cone shaped s.s. piece was inserted into the top of the centre tube, the purpose of these modifications being to improve the circulation.

The shaft is driven direct from a ½ H.P. D.C. motor in flame proof casing. Its speed is controlled by a starter and speed regulator, also in a flameproof case, on the nitration platform; an indicator lamp in the circuit shows when the motor is on. The speed variation is from 0 to 900 r.p.m., the stirrer being normally run at about 500 r.p.m.

The nitrator is fitted with two thermometers, a mercury-in-glass type in one of the outer tubes, and a Negretti & Zambra mercury-in-steel instrument, the bulb of which is located in the bottom of the nitrator. This has a trip mechanism incorporated in the case, which is mounted on the control panel, and gives warning of excess temperature by lighting a red lamp. It is set to operate at 20°C, the nitration temperature being 15°C.

Separator: The separator is an enclosed vessel, comprising two s.s. sections bolted together and sealed with lead in the manner described above.

The lower section is an inclined rectangular box, 12½" square x 2'11" (longside) and 12" (short side), the top flange being horizontal. It has a bottom run-off into which two side connections

/arc

are welded, a 3" diam. manhole in the lower end, and a blank flange on the opposite (long) side. It has no corrugated packing which is normally found in the N.G. plant, to assist separation, but a brine cooling coil was fitted into this part of the separator to control the waste acid temperature if necessary.

The upper section has the form of a rectangular pyramid, 12½" x 1'6" x 1'5" high. The acid and DEGN emulsion enters by two spray pipes which pass through one side just above the flange. Separation is observed through a long slit window of toughened glass on the front side, illuminated from a second circular window on the opposite side, through which shines a lamp in an enclosed flameproof fitting.

The upper section is surmounted by a glass lantern bolted on and sealed, into which the separated DEGN rises, overflowing at the top into a central tube. This delivers by way of a pivoted channel arm, into one or other of the two compartments of a s.s. dividing box, so that the stream of DEGN is directed either to the wash columns, or into one of the hand washing tanks.

The bottom run-off from the separator discharges into the drowning tank and is normally closed by a drowning flap similar to that of the nitrator. Separated waste acid leaves by one of the side outlets at the bottom and overflows into the overflow bowl, which is mounted on the wall behind the separator. The levels of the waste acid and DEGN overflows are such that the normal level of separation is visible in the window provided; this level can be controlled by a s.s. plug cock on the waste acid overflow. The other side outlet at the bottom of the separator is for emptying the vessel after closing down.

The blank flange in the lower section of the separator replaces a separate drowning out pipe for the contents of the upper part of the separator, which was supplied but is not fitted.

Two thermometers are provided; one is a mercury-in-glass thermometer which passes through the top of the lantern and records the temperature of the separated DEGN; the other is a Negretti and Zambra mercury-in-steel, which records the waste acid temperature. Its bulb is in the lower part of the separator; the case is mounted on the control panel and has an alarm trip and warning light set to operate at 20°C, the same as the nitrator.

Overflow bowl: Waste acid rises up a central tube and overflows into a s.s. bowl covered by a glass inspection dome. The acid flows from a bottom outlet to the waste acid air lift. A fume outlet and an overflow pipe are also provided. In N.G. manufacture the acid is diluted slightly with water at this point, to prevent after-separation; the DEGN acid is not diluted, since this is not desirable, and no after separation occurs because the acid is not stored for any time.

Prewash Columns. From the dividing box on the separator the acid DEGN runs into a s.s. rectangular box with a sloping bottom and a bottom outlet. The outlet is flanged to the top of the first wash column. On the side of the box is an overflow for wash liquor which discharges into a s.s. baffle tank and overflows from there to the air lift for prewash liquors. There is also a baffle in the box itself, to retain DEGN, and a brine cooling coil, to prevent the prewash liquor heating up. This is supported

/from

from a bolted-on lid which also has a socket for a mercury-in-steel dial thermometer, and a hinged inspection opening.

The washing columns, of which there are three, are 3" standard Pyrex glass pipe; the first and third are 2'6" long and contain 5 mesh s.s. trays which support layers of 3/8" glass beads; in these columns the flow is counter-current, the DEGN descending through the wash water which flows upwards. The middle column which is 3'0" long has a s.s. air injector at the bottom. This lifts DEGN from the bottom of the first column, and wash water upwards, so that the flow here is co-current.

The top of the second and third columns are connected by standard Pyrex Tee pieces; the DEGN falls into the third column and the wash liquor is returned by a PVC hose to the base of the first column.

The lower end of the third column is extended by a glass separating section, the bottom of which is closed by a s.s. flange with a central 1/4" outlet. It has a side inlet through which fresh wash water enters. A separation level is maintained below this point, by allowing the separated DEGN to overflow through a flexible tube attached to the bottom outlet, and raised to a height sufficient to balance the wash water in the column.

The overall effect of the washing unit is counter-current flow of DEGN and wash liquor, although the flow in the individual columns is alternately counter-current and co-current.

The wash water flow is regulated by a rotameter, 0.02 - 0.2 gals./min. with m.s. fittings, and the air, which is supplied from a reducing gauge at 20 lb./sq.in. is controlled by a screw clip. The air and water lines are taken up to a height above the top of the columns before connecting up, so as to prevent the DEGN and wash liquor from getting back into the supply lines.

Final Wash Columns. Originally the arrangement of the final washing columns was similar to that of the prewash columns, except that there were five columns instead of three, two co-current and three counter-current. The soda solution entered at the bottom of the third column, and the soft water at the bottom of the fifth column. The soft water, flowing back, diluted the soda solution which was supplied at a higher strength than required, to compensate for this dilution. The solutions were metered by rotameters of range 0.05 - 0.5 gals./min. The effluent discharged from the first column through the s.s. feed box passed through a lead baffle tank and thence to the Wash Water Settling House.

The separated DEGN collected at the bottom of the final column and was re-emulsified in an injector and lifted away into the washing tanks in the house. The s.s. injector was sealed down from the standard N.G. pattern transport injector; it was fed with soft water controlled by a valve and pressure gauge.

Fume disposal. Fume from the final wash columns is led by aluminium pipes flanged to the tops of the columns to a lead catchpot and thence evacuated to atmosphere, via a stack pipe, with an air injector to create the necessary vacuum.

/Fume

Fume from the nitrator, separator, dilution box, and pre-wash columns, is passed through s.s. piping to an earthenware Wolffs bottle, to trap DEGN vapour, and thence through a stone-ware absorption tower outside the mound, to remove acid vapours. Suction is maintained by an air injector on the absorption tower outlet.

Drowning Tank and Drowning Mechanism.

The drowning tank, which is 5' x 4' x 3' (360 gals.) is of sheet lead, draped on a steel frame. It stands under the nitrator platform and is positioned so that both nitrator and separator drowning tubes discharge into it. It is normally 2/3rd full of water and has an air agitation coil, and overflow and draining faucets. It is emptied through a labyrinth.

The drowning flaps are connected by rods and cranks to two independent drowning levers mounted side by side in a box frame on the nitrator platform. A third lever enables both flaps to be pulled simultaneously if required, as in an emergency. The flaps can also be operated by a wire and pulley system from either of the exit doors. Operation of the drowning levers simultaneously opens a quick acting valve, which puts air agitation on to the tank.

Air Lifts.

The waste acid and prewash liquor lines are connected to two air lifts in the traverse of the house. These are made of stainless steel and are the usual pattern used for acid work. The waste acid is lifted into a s.s. line from which it flows direct to the denitration feed tanks; the prewash liquor is returned by a second s.s. line to a mixing vessel in the Egg House, where it is fortified with C.O.V. and then elevated to the denitration feed tanks, this latter operation being an intermittent one.

The air lifts are operated with low pressure air at 2-5 lbs./sq. in. regulated from outside the house. The displacement acid left in the plant at the end of a run is also evacuated by the waste acid air lift. For this purpose the side drain connections at the lower end of the nitrator and separator drowning tubes are tee'd into the waste acid line from the overflow bowl.

Storage and Batch Washing House.

This is the No.1 Washing House described in Part III of this report. The batch washing tanks are used for the storage of DEGN from the Schmid plant and for further washing, if required. There are two tanks, each with a capacity of 1,000 lbs. DEGN. Smaller quantities of finished DEGN can be stored in the small hand washing tanks in the Schmid House, although the primary purpose of these is the emergency storage of unwashed DEGN from the separator, if the wash columns get out of balance and are taken off-stream temporarily. The combined capacity of these two tanks, which are of the conventional lead pattern, is 500 lbs. DEGN, plus wash water.

The washed and stabilised DEGN is filtered in the usual way through sponge filters, measured out in a 25 lb. lead M/G type burette, and stored in lacquered cans.

/Acid

Acid Recovery Plant.

The acid recovery is worked on a continuous basis and therefore forms an integral part of the process. The plant comprises essentially a steam heated Pauling type denitration still, 6" diam. x 9' high. It has duplicate lead feed tanks and feed boxes, a silica condensing coil, stoneware absorption towers, and a lead cooler for denitrated acid.

The waste acid from the nitration house collects in one of the feed tanks and is passed into the tower without delay through a siphon weir feed box. Fortified prewash liquor is fed from the second feed tank, this being filled intermittently from the mixing vessel in the Egg House.

The condensed strong nitric acid is collected direct in stainless steel drums ready for transit to the acid mixing plant, or storage. The denitrated sulphuric acid is also collected direct into drums, these being aluminium, coated internally with an acid proof paint. The weak acid is transported to the concentration plant and subsequently re-used as C.O.V.

Safety Devices.

Manual control is relied on, with the exception of the automatic warning devices listed under (B).

(A) Devices controlling supplies. The DEG supply can be instantly stopped by hand by closing the injector. The mixed acid is controlled by ordinary plug cocks.

(B) Alarms. Warning of excess temperature in nitrator and separator is given by red lamps operated by mercury trip switches incorporated in the Negretti & Zambra dial thermometers. The trips have to be reset by hand.

Warning of power failure is given by a lamp on the control panel. This is in the motor circuit and consequently is only on while the motor is receiving power.

(C) Drowning. This is effected by hand levers operated from the nitrator platform, and also by cord and pulley system from each of the doors.

/III.

III. Notes on Plant Design.

Nitrator: Being a scaled-down version of the standard 600 kgm/hr. Schmid nitrator, it was necessary to compromise with the significant dimensions in order to secure flow and heat transfer characteristics as close to the original as possible. The design adopted was based on a 4" central tube, and riser tubes of the same diameter as the original, i.e. 1" nominal tube (13/16" int. diam.) with 30 riser tubes, this gave a cooling surface of 1.8 sq. ft. for the down tube, and 10.9 sq. ft. for the riser tubes, total 12.7 sq. ft. With the stirrer speed adjusted to give a velocity in the riser tubes of 1 ft./sec. the velocity down the central tube is then 1.35 ft./sec. and the times of contact are respectively 1.75 secs. up and 1.28 secs. down. The ratio on the full scale plant is 2 ft./sec. in the down tube, for 1 ft./sec. in the riser tubes, and in the initial operation of the DEGN nitrator, the pull into the central tube was found to be insufficient, and a stagnant patch accumulated at the surface round the impellor shaft. This was cured by inserting a stainless steel conical rim into the top of the central tube which reduced the initial diameter of the tube from 4" to 3" and also reduced the clearance from the central tube to the surface, the net effect being to reduce the cross sectional area at this point, and increase the flow velocity.

Separator. This was supplied without the corrugated sheets normally fitted to the N.G. separators, and these do not seem to be necessary for DEGN waste acid.

It has not been necessary, with the acids encountered so far, to use the brine coil in the separator to prevent a temperature rise. It could, however, be used to cool the acid below nitrating temperature, and thus depress the solubility losses of DEGN in the acid.

Prewash columns. Except for some changes in the type of packing used in the counter-current columns, and the addition of a cooling coil in the off-take box for the acid wash liquor, the prewash columns have operated more or less as designed.

The packing originally used consisted of Stedman cones of stainless steel gauze, the intention being that DEGN would wet the cones in preference to water. However, this did not occur, and the resistance of the cones caused flooding; since the extraction was in any case efficient enough, the Stedman packing was replaced by a sieve-plate type packing, made with 8 mesh s.s. gauze.

When the amount of water admitted to the columns was reduced so as to produce acid liquors stronger than 30% HNO_3 , it was found impossible to keep the temperature of the final wash liquor below 40°C., and a cooling coil was fitted in the off-take box. This circulates brine, but the cooling required to hold the temperature down to 20°C. is not very great and cold water cooling would be satisfactory.

The design of the stainless steel end pieces at the bottom of the first column were modified so as to prevent the accumulation of stagnant DEGN.

/The

The final separating section for DLGN at the lower end of the last column is too small (capacity $1\frac{1}{2}$ lbs. DLGN) and the control of separation level is too sensitive. This should have a capacity of approx: 3-5 lb. separated DEGN.

Final Wash Columns. The original unit was designed on the same principle as the prewash columns, viz: alternate co- and counter-current columns, no separation being provided between the soda and final water columns. The final separating section was similar to that in the prewash columns.

In the presence of alkali, however, the DEGN persisted as an emulsion for longer than in the acid prewash column, and a proper flow of separated DEGN down the counter-current columns was not obtained. A fairly large separator is therefore necessary between the soda and final wash units, and also after the final wash unit, and these modifications are being made. As the N.G. type co-current columns have large intermediate separators and could be used without modification for DEGN washing, there is no need for extensive investigational work, but it would be advantageous to reduce the hold-up in the intermediate separators as far as possible. The Biazzi principle may be useful for this purpose.

The design adopted for the prewash unit is considered superior to the standard N.G. co-current towers, for deacidification, since it is necessary to work up the strength of the acid liquors, and this would require at least two standard N.G. co-current towers and intermediate separators, with backward feed of wash water.

/IV.

IV. Operation of Plant.

Five operatives are required to work the plant, one for nitration, one washing, one to maintain services, and two for the acid recovery plant. Their duties are clearly defined in the "Working Regulations" which each man is required to learn.

Prior to nitration, a number of tests are carried out by the nitrator attendant, under supervision. These consist of inspecting the empty nitrator and separator, testing both drowing mechanisms, checking the run-off cocks for smooth working, and testing the brine drum for leaks by expelling the brine and filling the drum with H.P. air.

Regulation and testing of the Arca l.p. air regulator is done by the scientist-in-charge.

To prepare for nitration, the services and supplies are opened up according to a definite schedule. The plant is ready for nitration to commence, when

- (a) all services and supplies are available.
- (b) the nitrator and separator have been filled with displacement acid and the displacement acid tank has been refilled.
- (c) the waste acid overflow cock is shut.
- (d) the DEG tank is on pressure.
- (e) the DEG and M/A rotameters and the DEG injectors have been tested and cleared of air locks.
- (f) the DEG has been circulated to bring its temperature to 20°C. in the delivery line to the injector.
- (g) the brine temperature is at -6°C. or lower.
- (h) the wash columns have been filled with wash solutions.

To commence nitration, the stirrer motor is started and adjusted to the normal operating speed (indicated by ammeter reading), the brine is cracked open, and the mixed acid flow is started. When the temperature has fallen to 10°C., the DEG injector is opened. When the DEG and M/A flows are steady, the temperature is allowed to rise to 15°C. and maintained by regulating the brine outlet valve. The DEG temperature is maintained at 20°C. by the warm water control valve.

About 40 mins. after starting nitration, sufficient DEGN will have collected in the separator, and waste acid is then allowed to overflow to the air lift, so as to maintain the separation level constant. At the same time, DEGN begins to overflow to the prewash column, and the wash water, air and brine on the prewash unit are opened up.

The wash liquor from the columns flows through the labyrinth tank and is taken away by air lift. The prewashed DEGN accumulates in the separating section after about 10 minutes, and is then allowed to overflow to the final wash unit, the supplies to

/which

which are then also opened up. When the washed DEGN separates at the end of this unit, water is turned on to the transport injector to take it away to storage.

To close down, first the DEG and then the Mixed Acid supplies are shut off, and the brine closed in. The waste acid overflow cock is shut and the stirrer motor is stopped. Displacement acid is admitted to the nitrator through the mixed acid rotameter at such a rate that the DEGN is displaced to the wash columns at approximately the normal rate. When all the DEGN has been displaced from both nitrator and separator, the displacement acid supply is shut off and the acid in both vessels run out through the bottom run off lines to the air lift. About 1 hour is required to empty both vessels by the air lift. The wash columns are kept in operation until all the DEGN has been passed through. The columns are then emptied from convenient low points and washed out to remove traces of DEGN. The wash liquor labyrinth is emptied and the air lifts drained. The nitrator and separator are washed out with water and allowed to drain into the drowning tank.

/V.

V. Operating Conditions.

1. Nitration and Separation. It was considered desirable when the plant was first operated to use a nitrating acid which gave a waste acid of more than adequate stability. The Woolwich nitrating acid, viz: 2.57 parts of 72/28 acid was therefore not used, since the waste acid has a life of only 3-6 hours. The acid used at Bomlitz, viz: 3.18 pts. of 62/35/3 acid, was used in the early runs; later the conditions were changed to 2.90 pts. of 65/35 acid. The resulting waste acids were known to have a life of at least 12-18 hours; actually they were found to remain stable for about 21 hours. The lowest acid ratio used up to the present is 2.80 parts of 65/35 acid.

The throughput times in the separator are 30 mins. for the DEGN and 90-100 mins. for the waste acid; very clear separation is obtained. Obviously the lowest permissible life for the waste acid is about 3 hours, without allowing any factor of safety. It is considered that an acid with a normal life of 6 hours probably represents the best compromise between economy and safety in working.

The nominal rate of production of 100 lb/hr. of washed product is attained without difficulty, the feed rates for this output being approx: 60 lb/hr. DEG and 170-190 lb/hr. mixed acid, depending on the ratio used. The brine temperature rises 5°C (9°F) and the overall heat transfer coefficient appears to be 50 BTU/sq.ft/ $^{\circ}\text{F}$ /hr, the quantity of brine used being 200-250 gals/hr. In an experiment to find the maximum throughput obtainable, it was found that above the feed rates corresponding to 125 lb/hr. of product, the nitration temperature could not be held down, although the brine was only warmed up $6-7^{\circ}\text{C}$. The limiting factors are therefore the overall heat transfer coefficient and the cooling surface available.

2. Prewashing. The quantity of water fed to the columns is calculated to yield a prewash liquor containing 43% HNO_3 , 6% DEGN (see Section V). Under these conditions, the acidity of the DEGN leaving the columns is found to be 0.1% HNO_3 , or less. The water feed rate for 100 lb/hr. output is 35 lb/hr (0.06 gals/minute). If the water rate is raised to 0.10-0.11 gals/min., corresponding to 30% HNO_3 in the prewash water, the acidity of the DEGN is reduced to 0.02% HNO_3 .

3. Alkali Washing. The DEGN produced from the final wash unit originally did not give a satisfactory Heat-Test, because of the failure of the DEGN to separate, and the imperfect washing which resulted. The heat tests obtained varied from $1\frac{1}{2}$ to 5 minutes. The improvement of this plant is still in hand, and no further results are so far available. Incompletely stabilized DEGN is given additional washes in the batch storage tanks.

4. Yields: The runs made up to the present have mostly been of 5 hours duration, and the yields assessed from this period of operation are necessarily lower than calculated yields because the DEGN lost in the displacement acid at the end of the run, is a significant fraction of the total yield. Yields between 87.0% and 87.4% have been obtained, and if these are corrected for the displacement acid loss, the gross yield, excluding working losses, is 89.5 - 89.9%, which agrees well with the calculated yields. These are set out in the flow sheets attached to this section and to Section V of the report.

TABLE 2.

Flow sheet for the Manufacture of DEGN b the Continuous (Schmid) Process (DEGN basis)

B. 2.70 parts of 69.C/29.5/1.5 Mixed Acid.

[illegible]

C. 2.90 parts 63/35 Mixed acid.

[illegible]

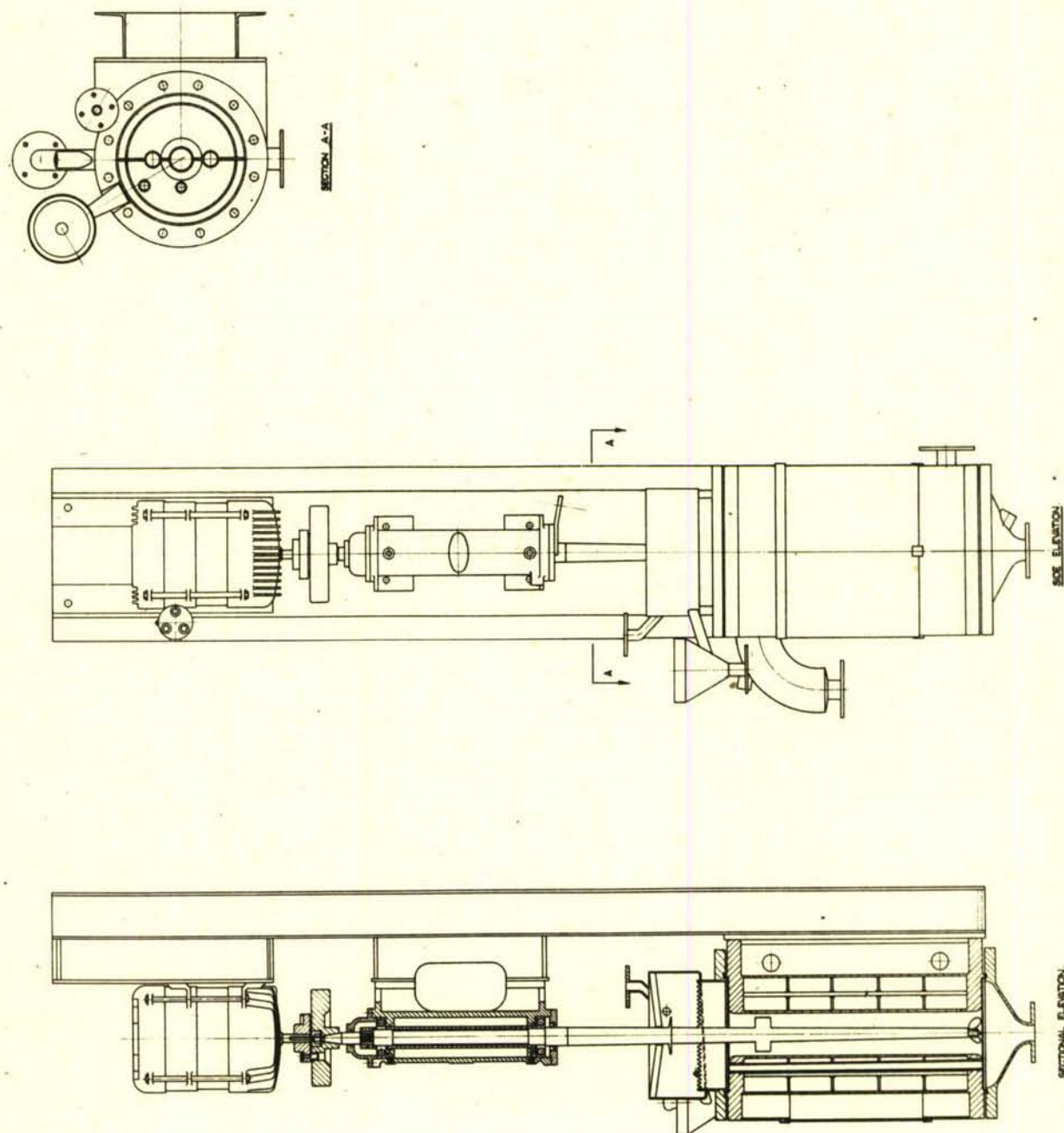
TABLE 4.

Flow Sheet for the Manufacture of DLGN by the Continuous (Schmid) Process (DLGN basis)

D. 3.18 parts 62/35/3 Mixed acid.

[illegible]

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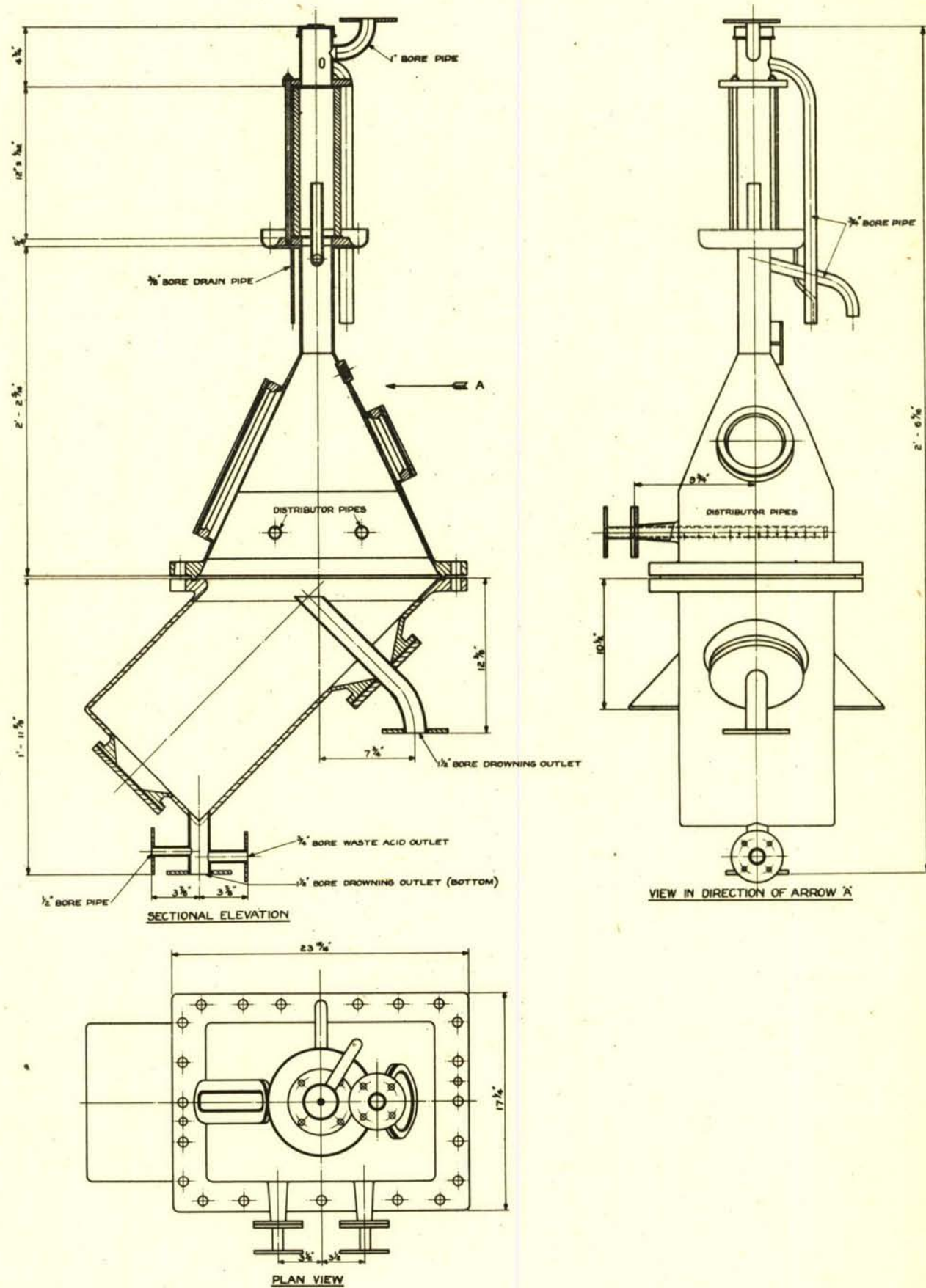


DRAWING No. 1

NITRATOR

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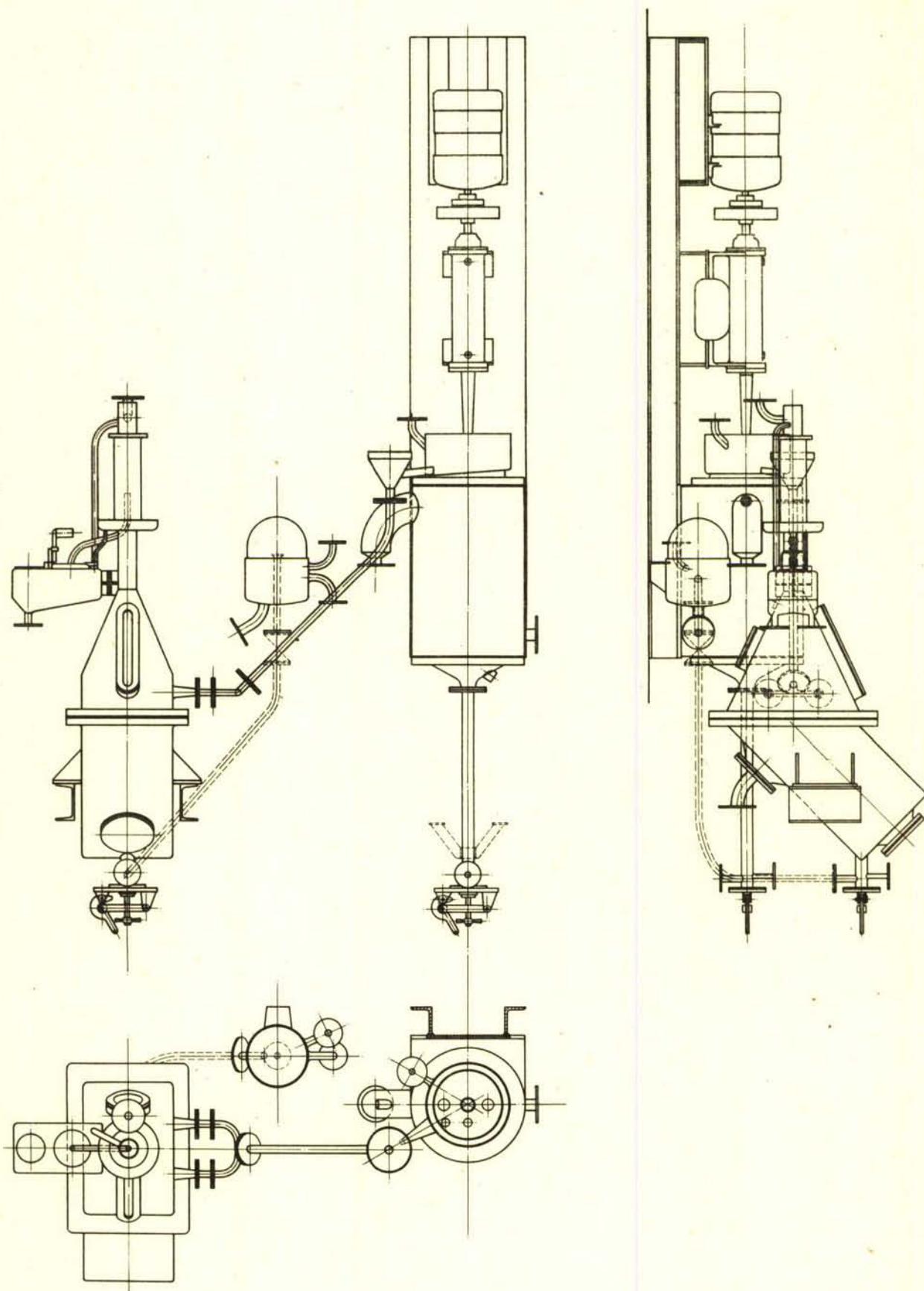


DRAWING No. 2

SEPARATOR

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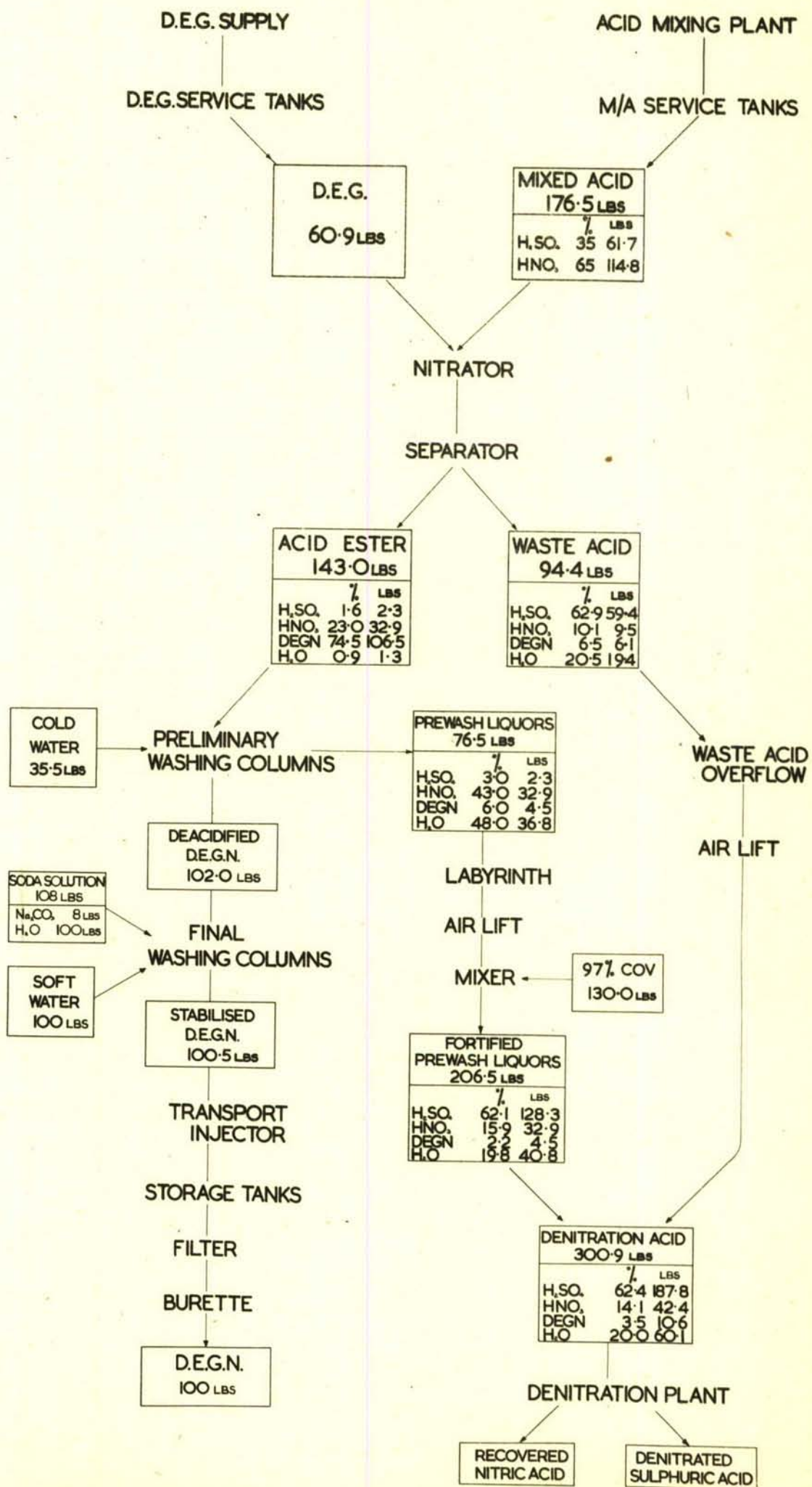
DRAWING No. 3

NITRATOR AND SEPARATOR - GENERAL ARRANGEMENT

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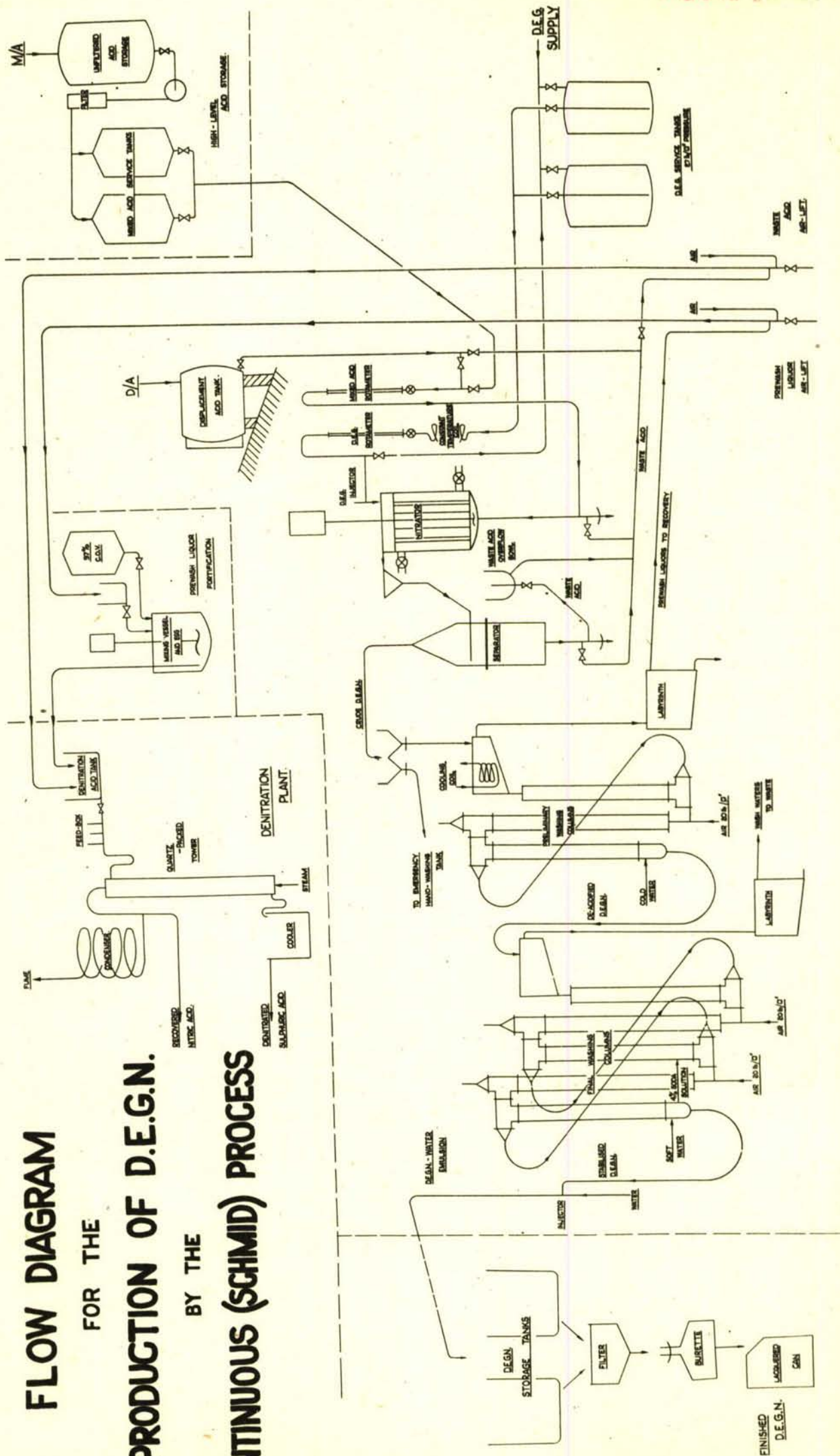
FLOW SHEET CONFIDENTIAL

FOR THE
PRODUCTION OF 100 lbs. D.E.G.N.



CONFIDENTIAL

FLOW DIAGRAM FOR THE PRODUCTION OF D.E.G.N. BY THE CONTINUOUS (SCHMID) PROCESS



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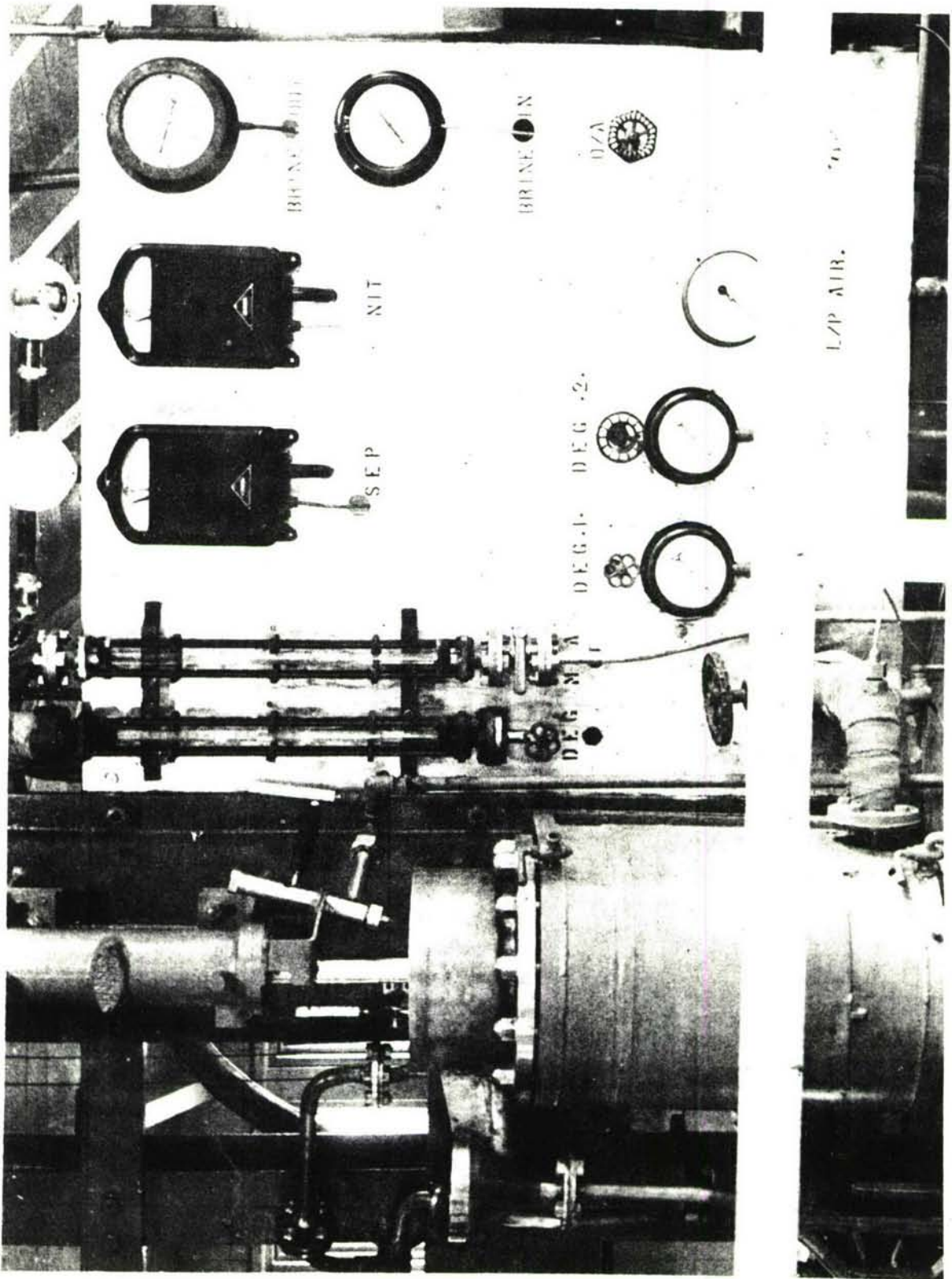


FIG. I. SCHMID PLANT - NITRATOR & CONTROL PANEL

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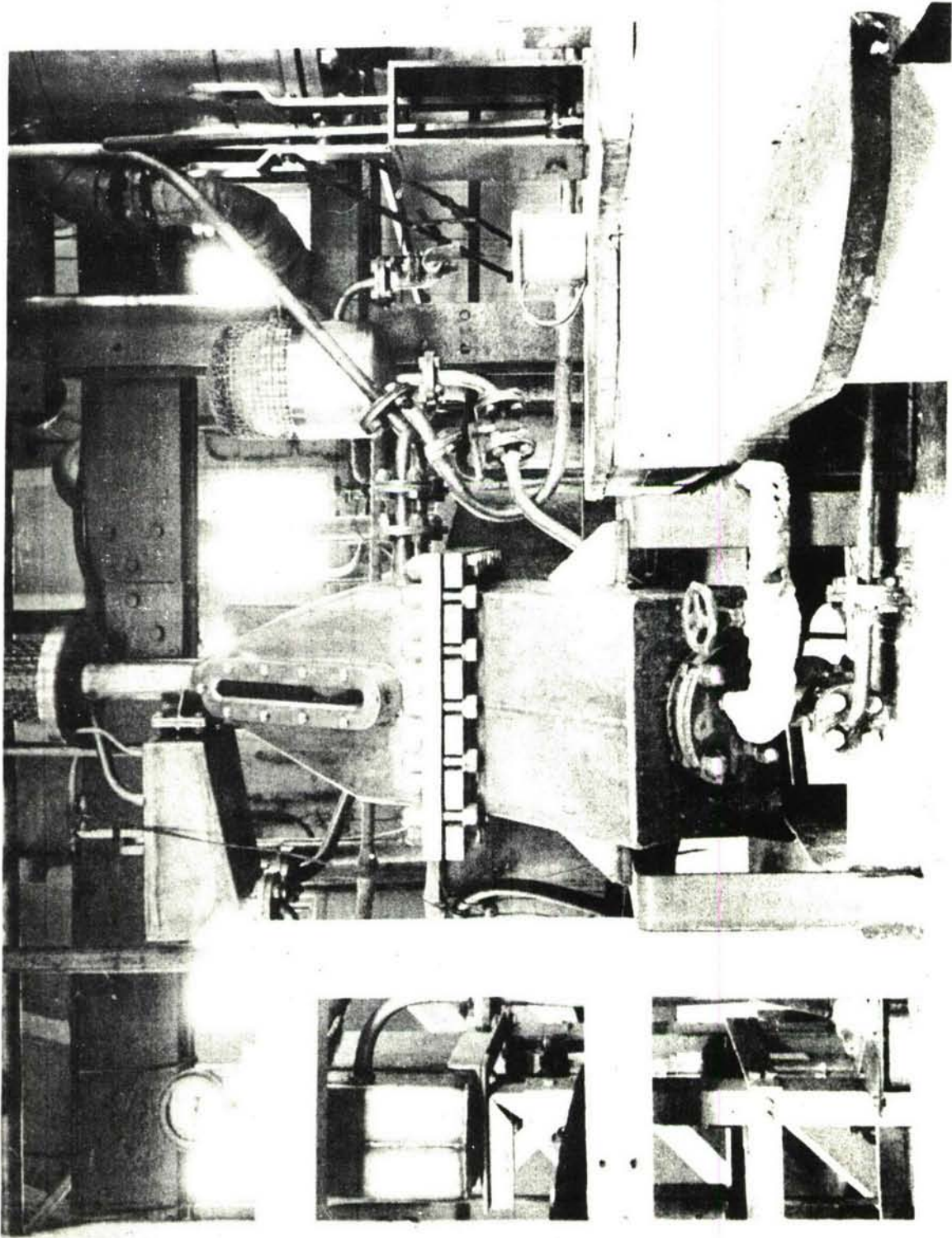


FIG. II. SCHMID PLANT - SEPARATOR.

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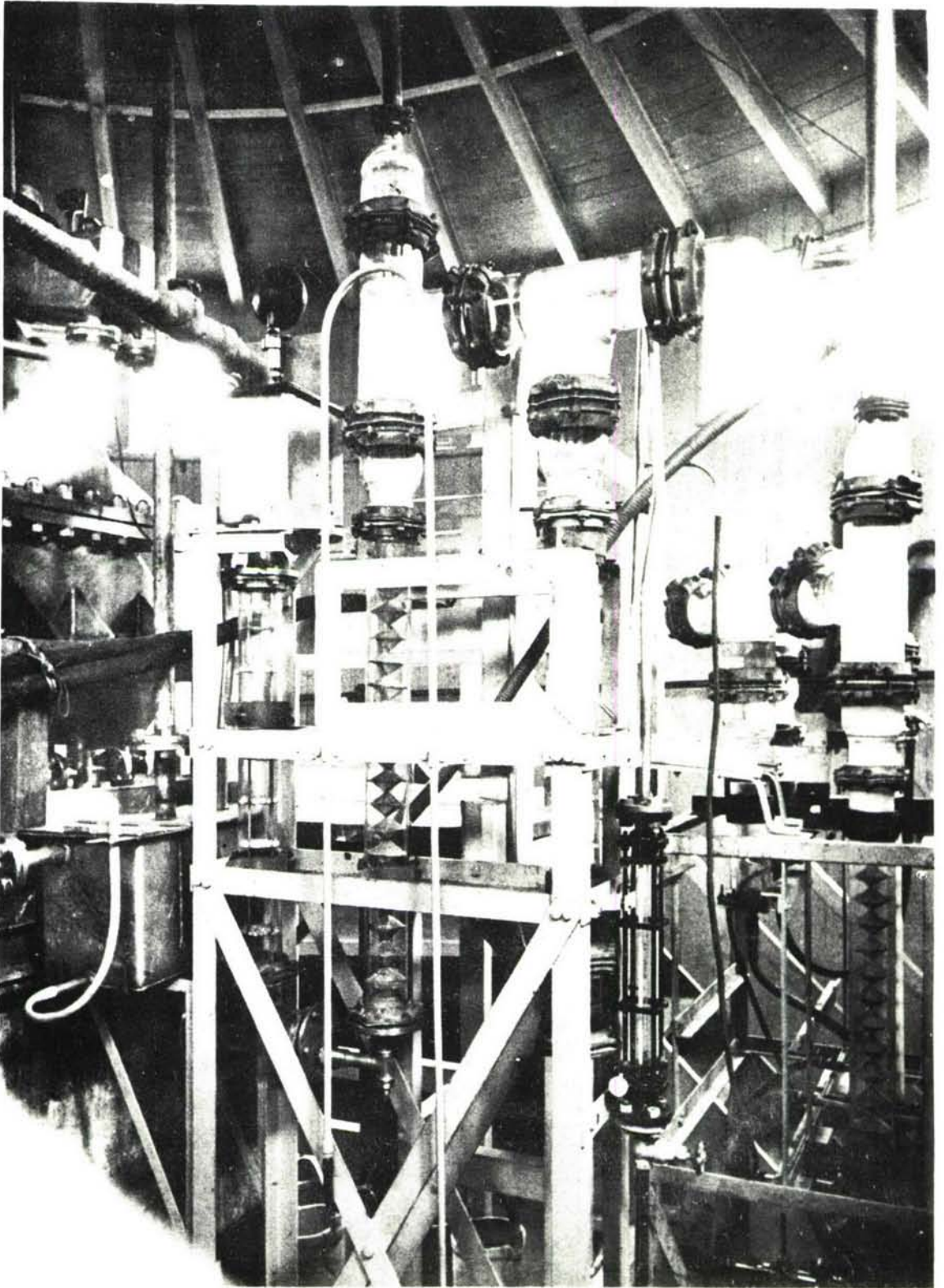


FIG. III. SCHMID PLANT - PREWASHING COLUMNS.

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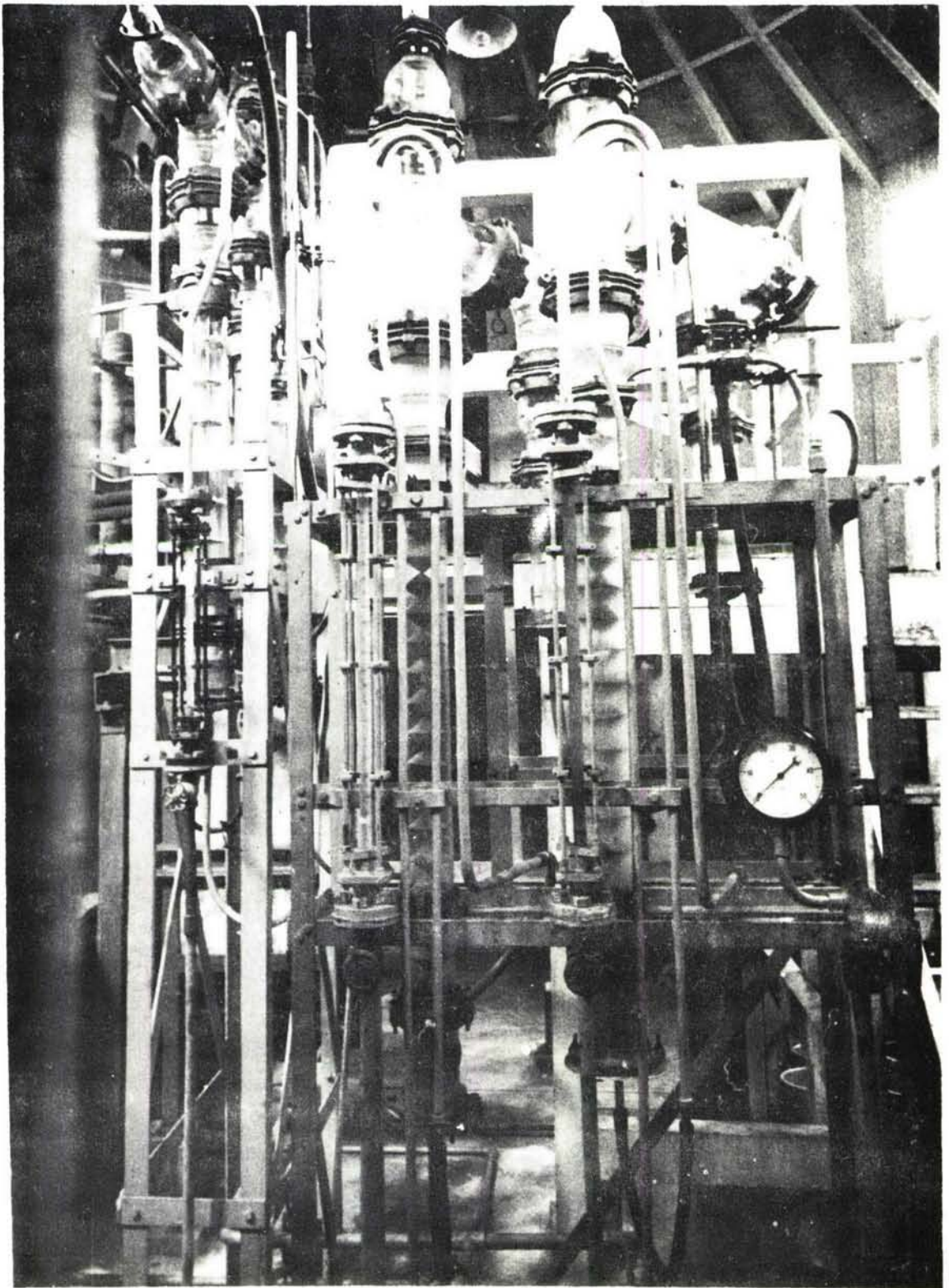


FIG. IV. SCHMID PLANT - FINAL WASH COLUMNS.

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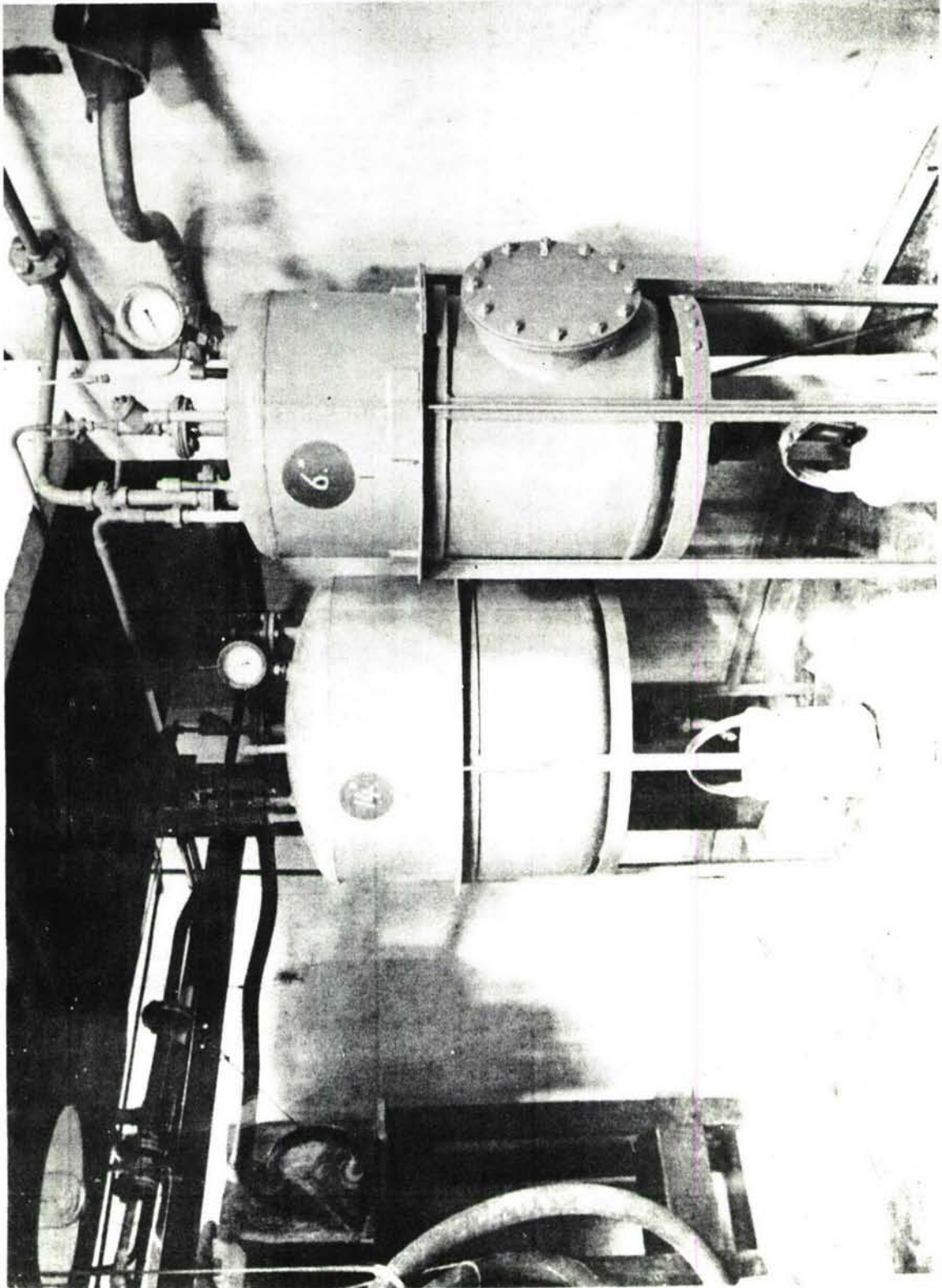


FIG. V. SCHMID PLANT - D.E.G. SUPPLY TANKS.

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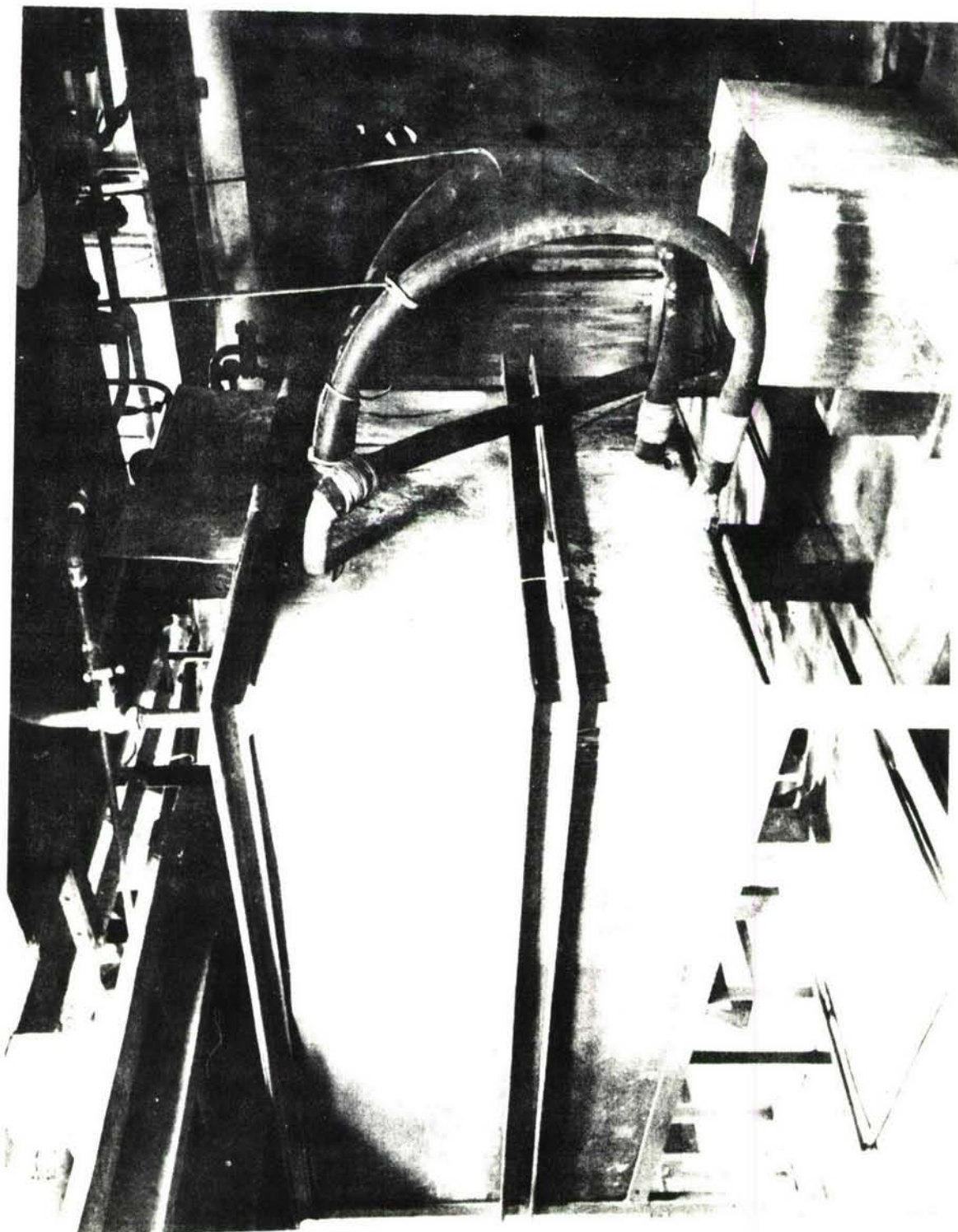


FIG. VI. SCHMID PLANT - DROWNING TANK.

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