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THE SPECTRUM OF FLUID FERTILIZERS

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Early Developments

Until about 1940, little had been done to develop liquid fertilizers. But from then to 1950, liquids became popular on the West Coast. The first standard liquid grade used was 8-24-0 or 9-28-0. During the last 15 years liquid fertilizer production has spread to practically every state and has become a rapidly expanding industry. The greatest production concentration is in the North Central states.[1]

The growth of liquid mixed fertilizer has been rapid but not as fast as for nitrogen solutions and ammonia. Figure 1 shows the trend in liquid mixed fertilizers.[2] Solutions and ammonia, for example, now supply 64 percent of the total straight nitrogen used; liquid mixed fertilizer supplies only about 6 percent of the mixed fertilizer demand. Together, they supply about one-fifth of the total nutrient consumption, a major accomplishment for an industry in only 20 years.[4]

Growth in nitrogen solution consumption has been particularly rapid in the Southeast; percentage increase since 1961 is 145 percent for the South Atlantic and 230 percent for the East South Central states, as compared with 100 percent for the United States.[2] Since the use of liquid mixes normally follows that of nitrogen solutions (the same storage, handling, and application equipment can be used), it is not surprising that use of liquid mixes is rapidly increasing in the Southeast.

Superphosphoric acid made from elemental P_4 was initiated by TVA in 1956. This acid will sequester (essentially dissolve) impurities precipitated when wet-process phosphoric acid is ammoniated.[3/] The use of superphosphoric acid stimulated an already rapidly growing industry. In 1957, the industry was geared almost entirely to the supply of surplus furnace acid not used in detergents and other relatively high-priced products. The less pure wet-process phosphoric acid, which is not as expensive to produce as furnace acid, found little use in liquid fertilizers.[5/]

TVA's research has shown that when wet-process acid is ammoniated in conjunction with superphosphoric acid or ammoniated superphosphoric acid (10-34-0 solution), the precipitation of impurities in the wet-process acid is greatly reduced or eliminated.[4/] Liquid fertilizers, almost free of solids, could be produced from wet-process acid because the polyphosphoric acids present in superphosphoric acid would sequester the impurities and retain them in solution. Formulations with 15 to 50 percent of the P_2O_5 from superphosphoric acid usually gives satisfactory sequestration depending upon the grade of the fertilizer produced and the purity of the wet-process acid. Grades high in potash usually require a greater proportion of superphosphoric acid.

Superphosphoric acid is also extensively used to produce base solutions such as 10-34-0 and 11-37-0. These solutions are used for direct application and to mix with nitrogen solution (32-0-0) and potash to produce N:P:K mixtures.

In 1960 TVA developed a process (which industry has accepted) for the production of superphosphoric acid from wet-process acid. Large amounts of wet-process superphosphoric acid have been used in the last few years to produce base solution 10-34-0. Small amounts have been used to sequester the impurities in wet-process phosphoric acids.

Liquid fertilizer-mix plants are generally of two types: liquid hot-mix or liquid cold-mix. In a liquid hot-mix plant, phosphoric acid is neutralized with aqua ammonia or anhydrous ammonia and chemical heat is released. In a liquid cold-mix plant, the raw materials used do not produce chemical heat when mixed.

Liquid Hot-Mix Plants

A typical liquid hot-mix plant is shown in Figure 2. In this plant, the liquid raw materials /phosphoric acid, aqua ammonia, urea-ammonium nitrate solution, and liquid base solution (10-34-0)/ are stored in tanks with capacities that usually range from 10,000 to 20,000 gallons. These tanks are made of carbon steel; however, the acid storage tank has a rubber or plastic lining. Solid raw materials (potash and urea) are stored in the building that houses the mix tank. The mix tank is usually of the batch type, and of 5- to 20-ton capacity. It is usually made of carbon steel but in some plants is made of stainless steel, or has a plastic liner.

The mix tank is usually equipped with a portable agitator and mounted on a scale; solid raw materials are weighed in it. The liquid raw materials are pumped from storage through meters to the mix tank. After the materials are mixed, the finished product is pumped from the mix tank to storage or nurse tanks.

In some liquid hot-mix plants, flow meters are not used. In such plants, the mix tank is mounted on a scale, and both liquids and solids are weighed, one at a time, in the tank. In other plants, liquids are measured in volumetric measuring tanks. A plant of either of these latter two types usually has production rates lower than a plant in which meters are used.

Liquid Cold-Mix Plants

In liquid cold-mix plants, a high phosphate liquid base solution, such as 10-34-0 or 11-37-0, is usually mixed with urea-ammonium nitrate solution (28, 30, or 32 percent nitrogen) and potash or a potash solution. A typical cold-mix plant is shown in Figure 3. In this plant, the liquids are weighed and mixed in a batch mix tank (usually 5-ton capacity) similar to that used in the hot-mix plant. Cooling equipment, acid storage tanks, and acid handling facilities are not required. Therefore, the investment cost for this plant is considerably less than that for the hot-mix plant.

Another typical liquid cold-mix plant is shown in Figure 4. This plant is so simple that it is usually referred to as a cold-blending station. Such a station usually has four storage tanks. Base solutions (10-34-0) and urea-ammonium nitrate solutions are stored in two of the tanks, while high-potash solutions, such as 3-9-9 and 4-10-10, are stored in the other two storage tanks. These potash solutions are usually produced in a centralized hot-mix plant and transported to the blending stations. The 10-34-0 and urea-ammonium nitrate solutions are shipped direct from the primary producer. The liquids are removed from storage using a pump. The desired quantity of each liquid is pumped through a meter into nurse tanks in which the mix is transported to the field.

Interest in suspension type fertilizers has increased mostly because of their potential use in the production of higher analysis liquid fertilizers and because suspensions serve as a carrier for secondary nutrients and micronutrients.

Suspension Fertilizers

A common definition of a suspension is that it is a fluid fertilizer containing solids, either soluble salts in a saturated solution or insoluble materials such as impurities from phosphoric acid and phosphate rock. Rapid settling of solids can be delayed by the addition of an inexpensive suspending agent. The suspending agents TVA uses extensively are gelling type Attapulgite clays mined in the southeastern United States. When this clay gels, it increases the viscosity and prevents the settling of crystals from the system.[6] Crystals or particles composing the suspension should be less than 0.03 of an inch in diameter (size of the openings in a standard 20-mesh screen) and suspensions in storage should be periodically air sparged to prevent the formation of a compacted layer. TVA is now using in process and product improvement programs a base suspension produced from superphosphoric acid and ammonia and containing 3 percent by weight of gelling clay. This base suspension is used in cold-mix plants to produce high-analysis grades. The following tabulation compares typical ratios of clear liquids, suspensions, and solid fertilizers.

Typical Analysis of Clear Liquid, Suspension, and Solid Fertilizers

Ratio	Clear	Suspension*	Solid
3:1:0	24-8-0	27-9-0	30-10-0
2:1:0	22-11-0	26-13-0	28-14-0
1:1:0	19-19-0	21-21-0	25-25-0
1:1:1	8-8-8	15-15-15	15-15-15
1:2:2	5-10-10	10-20-20	10-20-20
1:3:1	7-21-7	10-30-10	10-30-10
1:3:2	5-15-10	9-27-18	10-30-20
1:3:3	3-9-9	7-21-21	8-24-24

*Suspension fertilizers made with TVA 12-40-0 base suspension, 32-0-0, and 0-0-62.

The suspension fertilizers shown in this slide were produced from a base suspension 12-40-0, and they contain 11 to 133 percent more plant nutrients than clear liquids of corresponding ratios. The greatest increase is usually in the high potash ratios. The attainment of high-analysis fluid fertilizers is possible by using a base suspension which contains a high percentage of its P_2O_5 as condensed phosphates, primarily the highly soluble pyrophosphates and a suspending agent such as Attapulgite clay to support additives such as potassium chloride. These suspension mixtures were produced by cold mixing TVA 12-40-0 base suspension, urea-ammonium nitrate solution, and potash. They are produced in a conventional cold-mix plant such as the plant shown in Figure 5.

Most liquid fertilizers are limited by their solubilities, and generally only trace quantities of second nutrients or micronutrients can be added. With suspension, micronutrients, or secondary nutrients, can be added until the viscosity of the final product limits further additions.

Table 1 shows the quantities of micronutrients added to a 15-15-15 suspension made by using TVA base suspension 12-40-0, urea-ammonium nitrate solution, and potassium chloride. Micronutrients used in these suspensions are usually from a relatively inexpensive source.

Superphosphoric acid base suspensions contain more salts in solution; therefore, the suspending load for the gelling clay is less for them than for other types of suspensions. For this reason, these base suspensions should be more desirable than suspensions produced from other materials of lower solubilities.

TVA and others have studied the production of suspension fertilizers from wet-process orthophosphoric acid, triple superphosphate, nitric acid and phosphate rock, superphosphoric acid, urea and ammonium nitrate.[7]

A suspension made using wet-process phosphoric acid involves continued ammoniation of the acid at a pH of 7.5 to 8.5 and on completion of ammoniation the pH is reduced by the addition of phosphoric acid. During ammoniation the temperature is maintained below 160° F. and then dropped to 100° or less before the supplemental nitrogen and potash are added.[7] When the impurity level in the acid fluctuates, the viscosity varies; therefore, to produce a more stable suspension, a gelling clay is added. This described procedure has not been tested on commercial scale and was originally aimed at suspending impurities precipitated from ammoniated wet-process orthophosphoric acid.

Triple superphosphate suspensions involve the cold-mixing of superphosphate fines with urea-ammonium nitrate solutions and potash. The superphosphates can be ammoniated to use a relatively low-cost ammoniacal nitrogen and to increase the pH to reduce corrosion. TVA research showed the degree of ammoniation of the superphosphate and the order in which the ingredients were added to the mix tank had an important effect on the stability and viscosity of the suspension.[8] Another producer, manufacturing a superphosphate suspension, uses urea, potassium chloride, hot water, and a Bentonite clay. The pre-gelled clay is added to the hot water in the mixing tank. The urea is then added and the endothermic reaction reduces the temperature; then the superphosphate is added. The temperature of the slurry is 80° F. or lower when the potassium chloride is added.

Nitric phosphate suspensions, common in the Southwest and Midwest, are produced by reacting phosphate rock with nitric acid which forms calcium nitrate and phosphoric acid. A big problem in making nitric phosphate suspensions is ammoniation without losing citrate solubility of the phosphate. When ammonia is added, the calcium nitrate is converted to ammonium nitrate and the phosphoric acid forms dicalcium phosphate. When the pH is about 1.0, the availability is good but as the pH is raised more phosphoric or sulfuric acid is required to avoid formation of fluorapatite $Ca_{10}F_2(PO_4)_6$. Tests at TVA have shown that by supplying 24 percent of the P_2O_5 from 11-37-0 good availability was obtained when the pH was raised to neutral.[2]

Nitrogen suspension (37-0-0) is a suspension fertilizer containing more nitrogen than solid ammonium nitrate. This suspension is produced by combining urea, ammonium nitrate, and water at elevated temperature. When cooled, the urea crystallizes in a very finely divided form as the solid suspended phase.[3] One percent gelling clay is added to the suspension. This suspension can be used for direct field application or in combination with TVA 12-40-0 base suspension. The 37-0-0 is available in limited quantities only, but commercial producers have used 37-0-0 to manufacture such grades as 30-10-0, 20-10-10, 13-26-13, 16-16-16, 13-13-26, and 18-18-9. These formulations contain clay in excess of 1 percent by combination of clay from the 12-40-0 and 37-0-0.[2]

Another recent development is use of free-ammonia suspensions. In early work at TVA (1957) phosphoric acid was reacted with ammoniating solution to give high-nitrogen suspensions containing free ammonia. Under the test conditions, 7.5 to 10 percent P_2O_5 was the maximum for good fluidity and a typical product was 34-7.5-0. In such products, all the P_2O_5 is in the solid form, as triammonium phosphate. More recently, free ammonia suspensions made from anhydrous ammonia have been produced commercially. A typical grade of this type is 18-9-0. The main advantage is the low formulation cost resulting from use of anhydrous ammonia, but the cost of application is higher because the suspensions must be injected under the soil surface.[2/]

A typical application truck for broadcasting suspensions is shown in Figure 6. The tank is equipped with a transfer pump, bypass recirculation line, pressure gauge, and a boom with several flooding nozzles. The application rate is controlled by the pressure of the liquid to the nozzles. The pressure depends on the amount of liquid recirculated to the application tank.

Field tests have shown that there are much fewer plugging problems with these nozzles (Figure 6) than with other types. Recently, TVA tested the broadcast application of suspension fertilizers using an air compressor to supply compressed air for sparging the suspension fertilizer and to provide pressure to broadcast the suspension over a 40-foot swath. The application rate is controlled by the air pressure in the tank and the height and size of the nozzle. Agitation by air sparging is continuous. The excess pressure is routed to atmosphere through a hand-controlled valve. This applicator is shown in Figure 7.

Field tests have shown also that row-application equipment that uses a positive displacement pump such as a squeeze pump or a piston-type metering pump can apply suspensions with little or no difficulty.

Figure 8 is a sketch of this type of row application equipment with a squeeze pump. Some suspension fertilizer manufacturers have made extensive tests with this type of pump and have found that it applies suspensions with little or no difficulty.

For the past three years one suspension fertilizer producer has successfully used an aqua ammonia pump to row apply superphosphate suspension with sugar can seedlings (cut sections). Some manufacturers use slinger-type application equipment in broadcasting suspension fertilizers. An equipment manufacturer has recently designed more reliable and simplified slinger-type equipment. Figure 9 is a cut-away sketch of this type of equipment (John Blue Company slinger-type equipment). An agitator in the shape of a sweeping baffle is used to agitate the liquid in the application tank. The slinger mechanism is designed so that as it rotates, it also causes the material to be pumped from the tank of the applicator. This type of applicator will apply even the most difficult-to-handle suspensions.

Crystal growth and settling during prolonged storage are still problems and may be key factors in determining the future of suspensions.[9] However, the recent trend toward larger, more mechanized farms, the incorporation of secondary nutrients and micronutrients and selected herbicides and insecticides, and the ease of transferring and field applying suspension fertilizers with the equipment described above, should increase the demand for suspension fertilizers.

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Table 1

Addition of Micronutrients to Suspension Fertilizers

Micronutrient compound	Pounds added/ton of 15-15-15	Percent of element in product	Properties of Products at 75° F.			
			Apparent viscosity of fresh product, centipoises	After aging 1 day		
				Apparent viscosity, centipoises[a]	Percent	
					Settled	Pourable
No micronutrient	-	-	256	500	0	95
Sodium borate ($Na_2B_4O_7 \cdot 5H_2O$; 14.3% B all 20-mesh, 14.6% 100-mesh)	50	0.35	228	380	0	96
	75	0.52	248	-[b]	0	0
Copper sulfate ($CuSO_4 \cdot 5H_2O$; 25.2% Cu; all 20-mesh)	100	1.2	204	280	2	97
	150	1.8	200	-[b]	0	0
Iron sulfate [$Fe_2(SO_4)_3 \cdot 9H_2O$; 20.4% Fe; all 35-mesh]	125	1.2	200	380	0	96
	150	1.4	268	-[b]	0	0
Manganese sulfate ($MNSO_4 \cdot xH_2O$; 27.25% Mn; all 35-mesh)	25	0.34	236	360	0	98
	50	0.67	236	-[b]	0	0
Zinc sulfate ($ZnSO_4$; 36% Zn; 97% 100-mesh)	150	2.5	236	510	0	95
	200	3.6	308	1100	0	93
Mixture of above salts	150	0.1 B 0.2 Cu 0.6 Fe 0.6 Mn 0.3 Zn	200	470	0	96

a. After pouring twice.
b. Too viscous to pour.

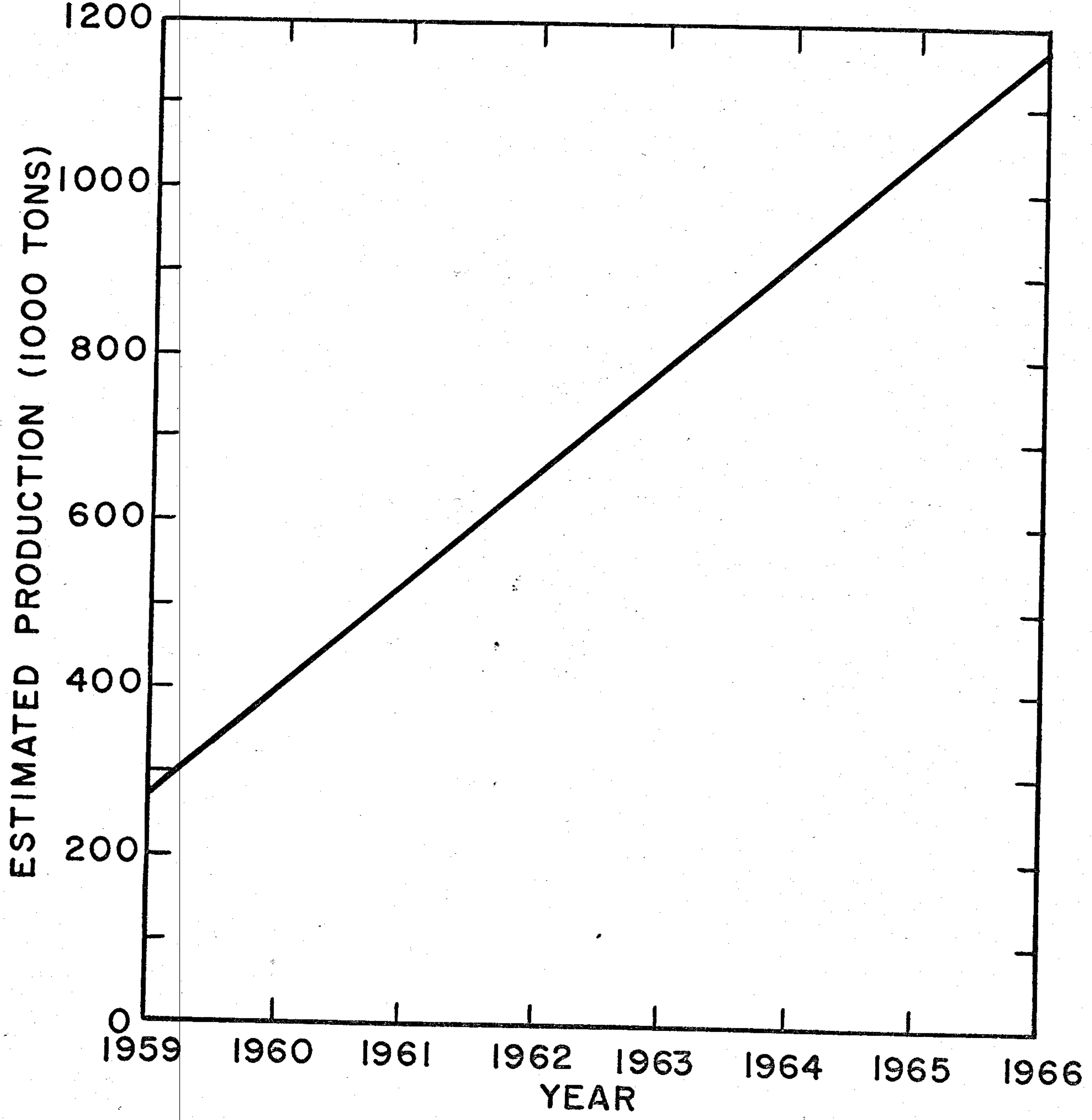


FIGURE I
APPROXIMATE ANNUAL PRODUCTION
LIQUID MIXED FERTILIZERS 1959-1966

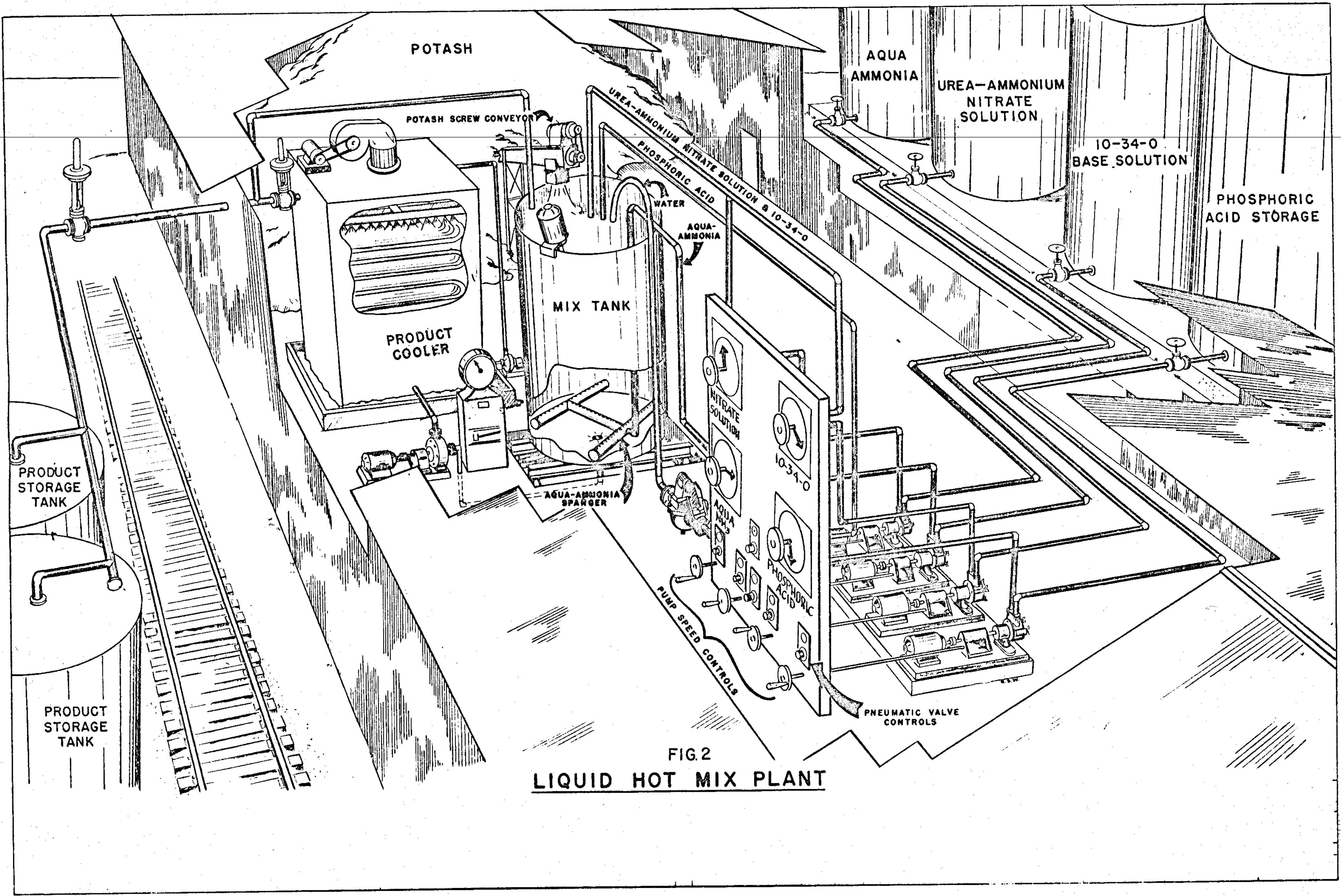


FIG. 2

LIQUID HOT MIX PLANT

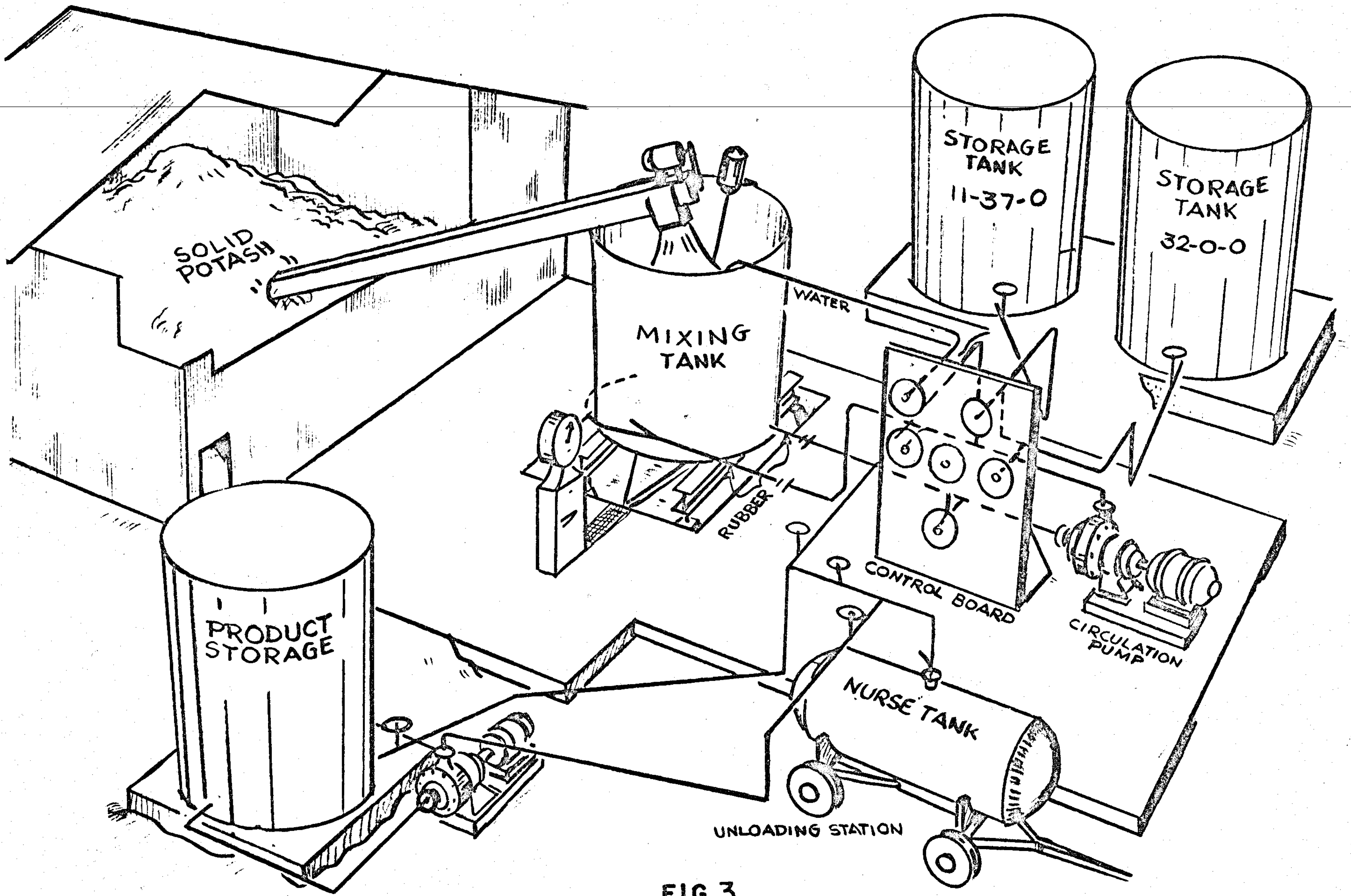


FIG. 3
LIQUID COLD-MIX PLANT

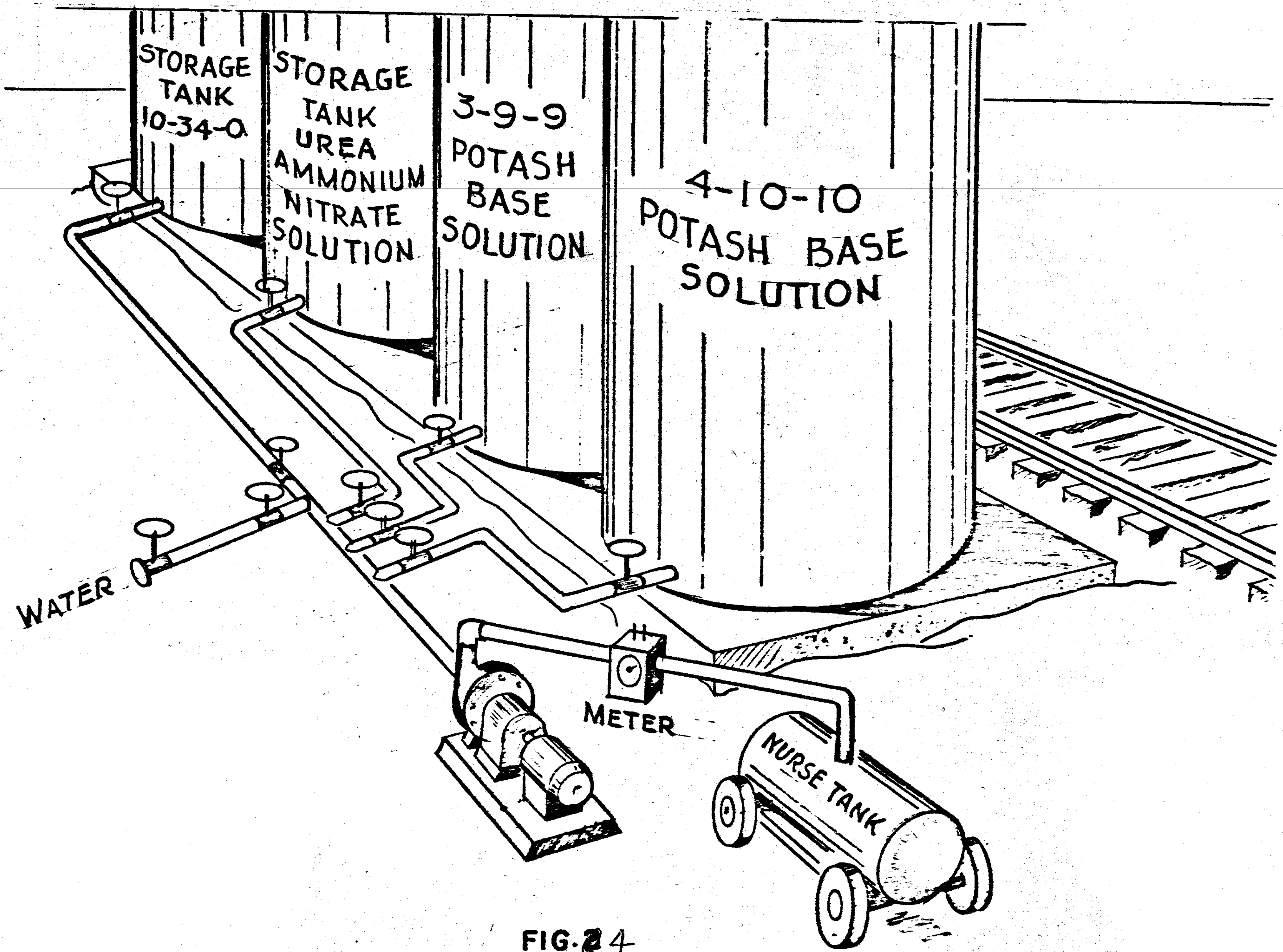


FIG. ~~2~~4

LIQUID SATELLITE STATION

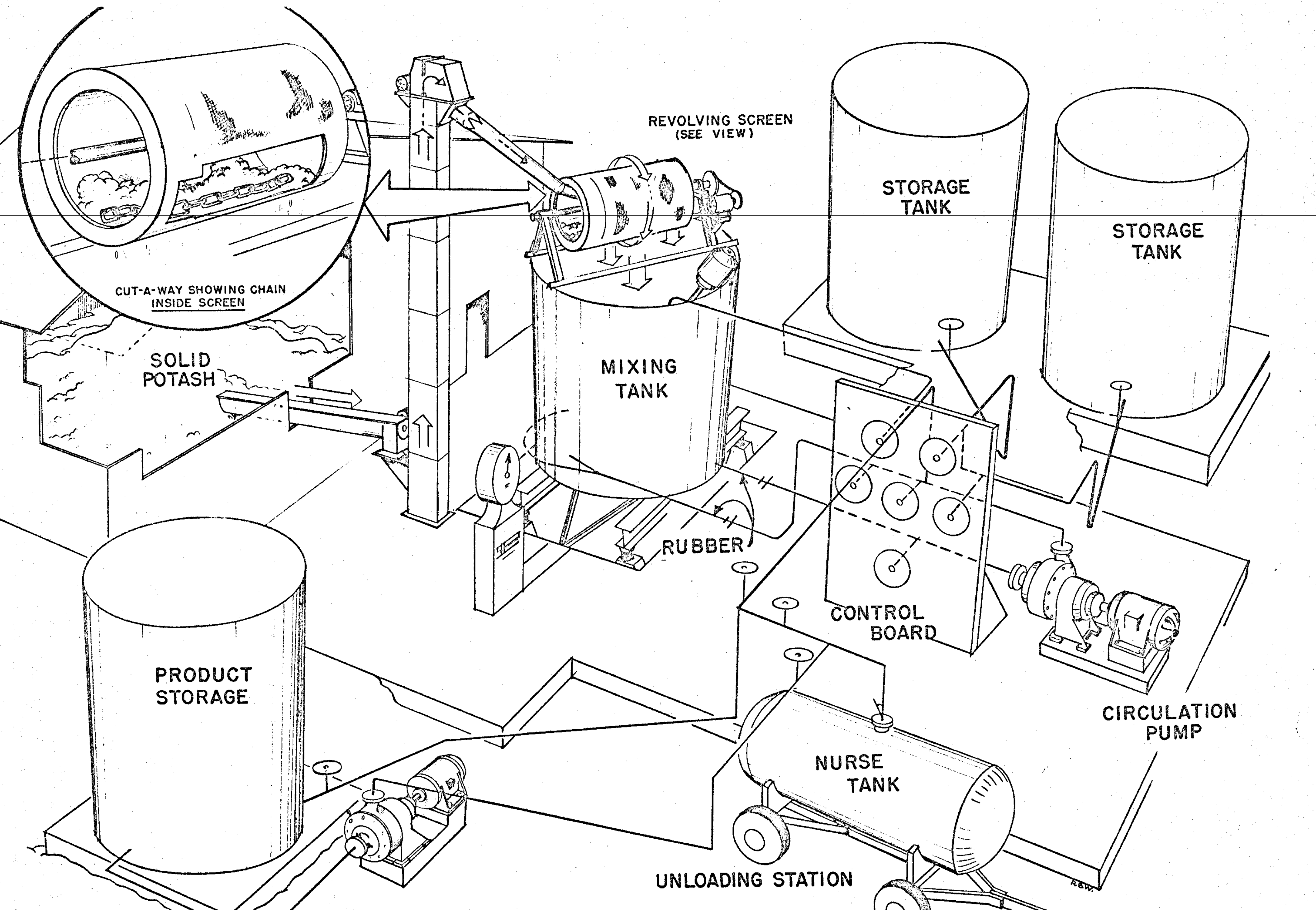


FIGURE 5

LIQUID COLD MIX SUSPENSION PLANT

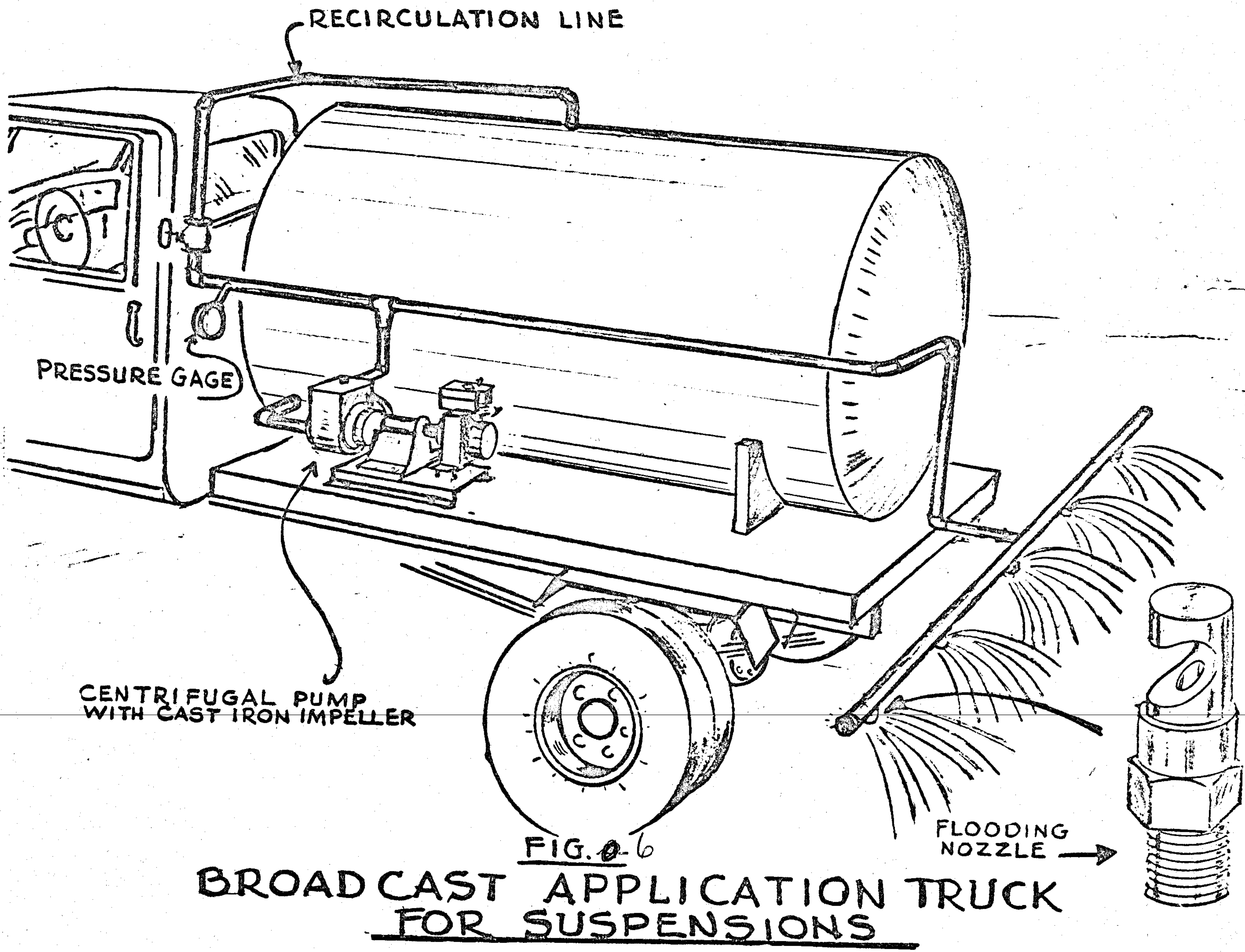


FIG. ~~0~~ 6

BROADCAST APPLICATION TRUCK FOR SUSPENSIONS

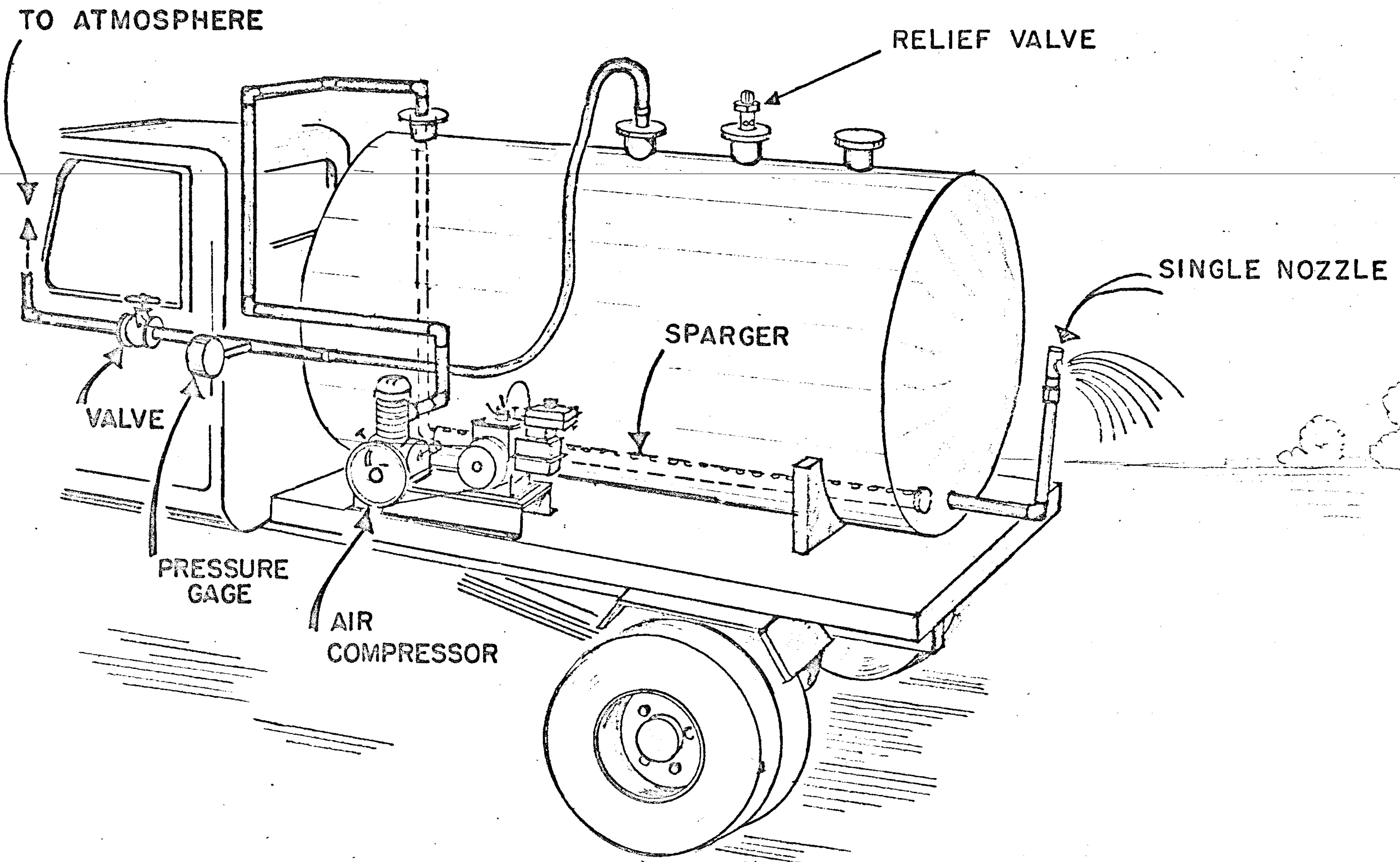


Figure ~~10~~ 7

BROADCAST APPLICATION TRUCK
FOR SUSPENSIONS

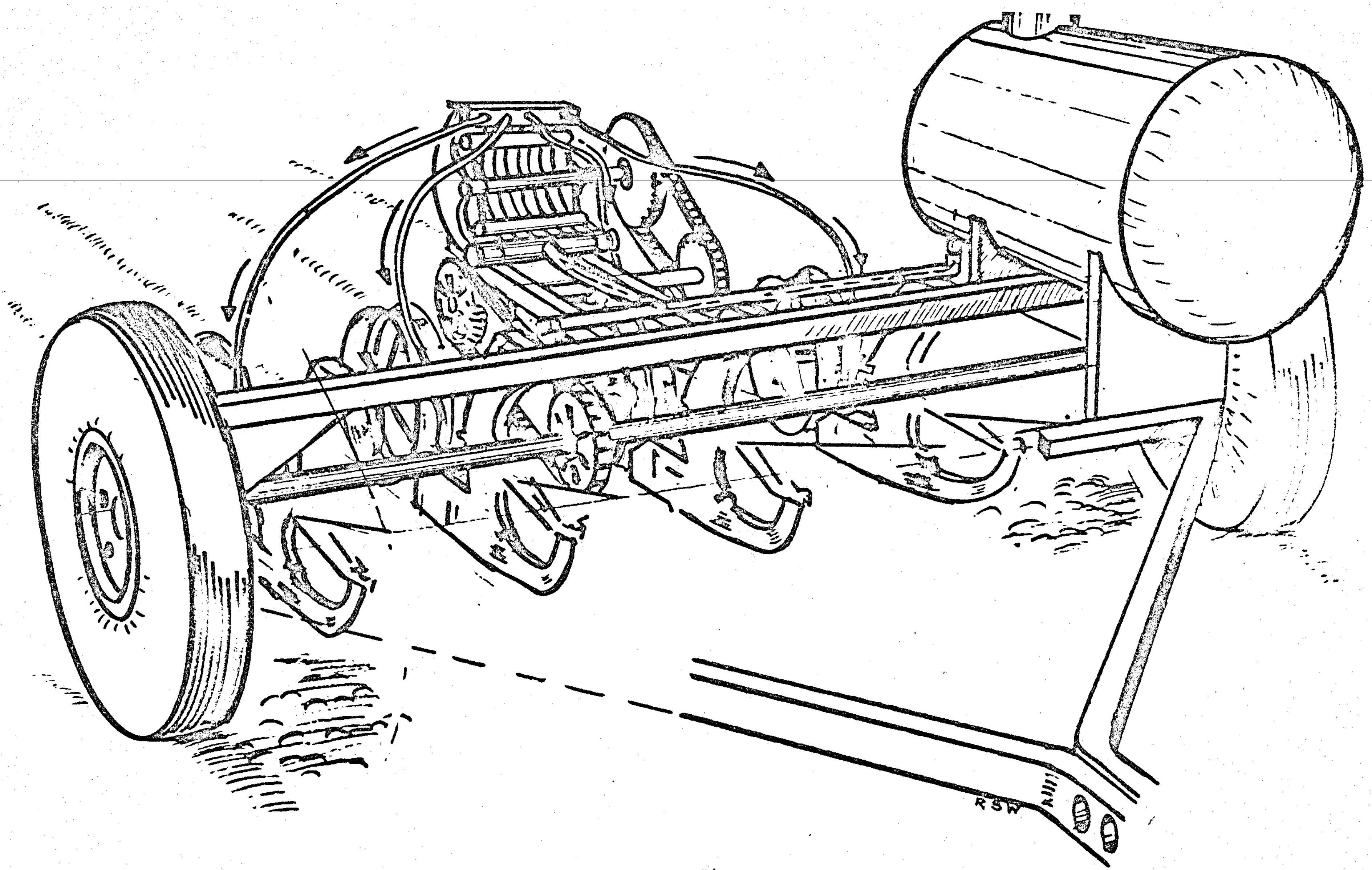
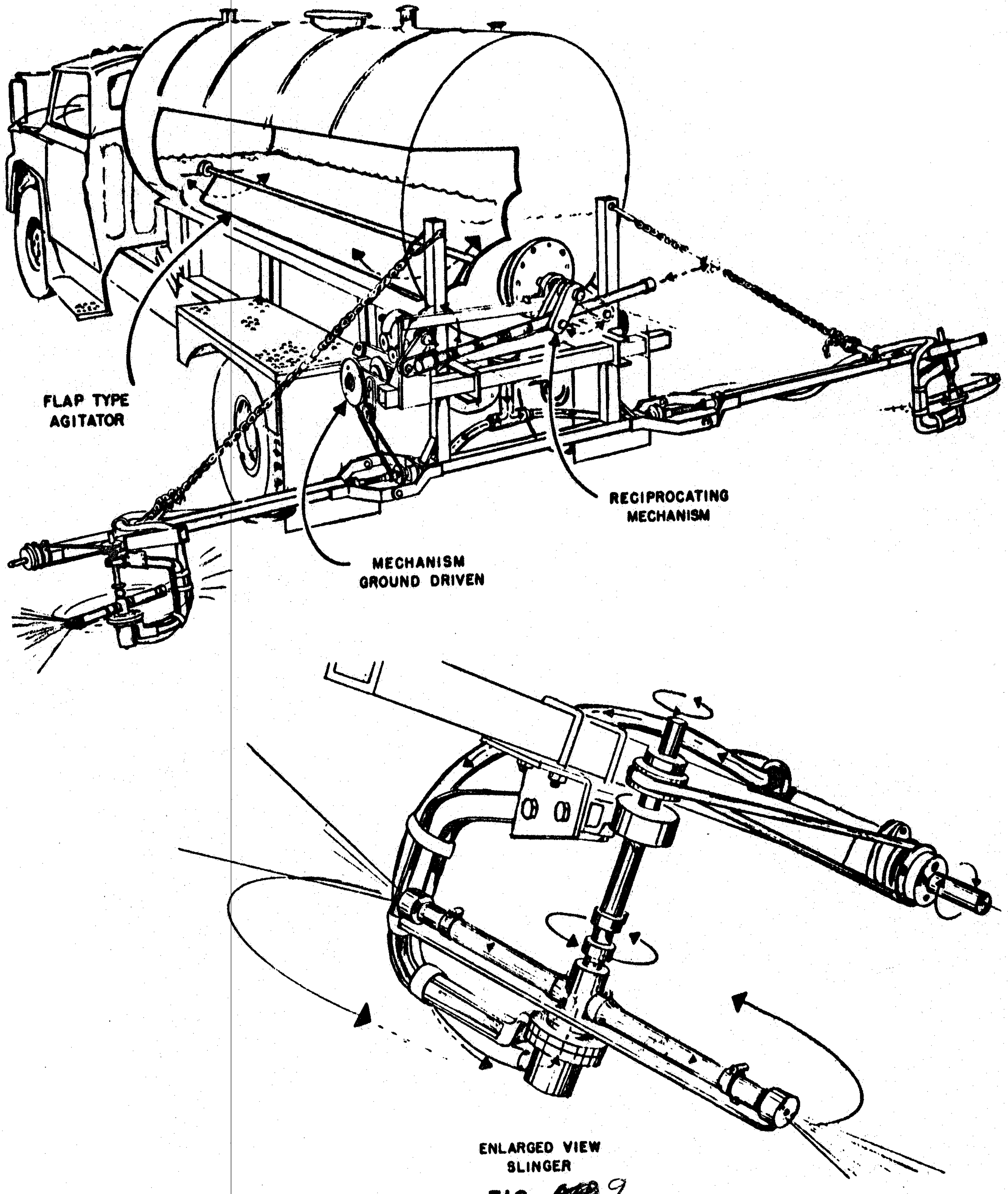


FIGURE 7

PLANTER ATTACHMENT
FOR SUSPENSIONS



ENLARGED VIEW
SLINGER

FIG. 9
SLINGER TYPE APPLICATOR