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Reduction of Air Emissions from Gasoline Storage Tanks

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Reduction of Air Emissions from Gasoline Storage Tanks

by

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ABSTRACT

The purpose of the project was to determine the technical and economic feasibility of the use of flexible plastic membranes as a mean to control emissions emanating from gasoline storage tanks. The emission rates and the expected life of the membranes were to be established.

A demonstration pilot unit was built and operated. The emission rates were determined, as well as the life expectancy of the membranes.

The results obtained indicate that emission control of better than 99% when compared to uncontrolled tanks can readily be achieved and that the life expectancy of the membranes is in the order of 20 years of continuous service.

The installed cost of these devices for commercial size applications has been estimated and found to be very competitive with the conventionally used floating roofs.

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SECTION I

CONCLUSIONS

1. From the data obtained during the operation of the demonstration pilot unit, it has been concluded that emission control efficiencies of better than 99% can readily be achieved when compared to uncontrolled tanks.

2. The emission rates remained essentially constant and independent of time.

3. The emission rates for dynamic operation of the storage tanks were found to be larger than the emission rates for static storage operation. A storage tank whose contents are subjected for extended periods of time to successive and contiguous cycles of filling and emptying is said to be under dynamic operation. A storage tank whose contents are withdrawn and refilled infrequently is said to be under static operation. The emission rate under dynamic operation is due to gas permeation through the membranes and to gas leakage through fissures and other imperfections in the attachment areas of the membranes to the tank. The emission rate under static operation is essentially controlled by gas permeation.

4. The life expentancy for the membranes is in the order of 20 years of continuous service.

5. The installed cost of these devices for commercial size applications are very competitive with the conventionally used floating roofs.

SECTION II

INTRODUCTION

The purpose of the project was to determine the technical and economic feasibility of the use of flexible plastic membranes as a means to control emissions emanating from storage tanks, holding gasoline and similar products. One of the goals set at the outset of this program was to provide an emission control greater than 95% when compared to uncontrolled tanks. Another goal was to establish the expected life of the flexible membranes under actual operating conditions, which is closely related to the economical feasibility. The technology required for the project at hand was made available by the Stop-Los Company, who is the originator of this technology, and in which it owns propietary rights.

The emission rates from gasoline storage to be expected were known beforehand for the materials to be utilized in the construction of the flexible membranes. However, this knowledge was restricted to a static system, i.e.- a device built according to the principles of this technology where the liquid stored would be kept in the tank without adding or withdrawing liquid at frequent intervals. The effect on the flexible membranes of a frequent cycling, for an extended period of time, and its consequences, if any, on the emission rates was one of the paramount objectives of this project.

With the previously cited objectives and goals in mind, a demonstration pilot unit was built and operated by the Stop-Los Company under a contract with the U.S. Environment Protection Agency. The following Sections of this report contain a detailed description of this effort.

SECTION III

EQUIPMENT AND OPERATION

The demonstration unit consisted of two vertical tanks of about 1300 gallons capacity each, fitted internally with flexible membranes or liners, a circulating pump for transfering the liquid between the tanks, piping, control valves, and two bladders.

The tanks were filled approximately half-way with water (saturated with gasoline) on which a layer of about 1" thick of gasoline was added. The water was transferred back and forth between the tanks by the circulating pump, thus raising the liquid level in one tank while simultaneously lowering it in the other.

The upper and lower operating levels were maintained by level controls electrically interlocked with the control valves. The filling and emptying of the tanks, between the selected liquid levels, was performed automatically and continuously at a relatively high frequency. The time required for one cycle (filling and emptying) was 36 minutes. The flexible membranes were thus subjected to the same range of cyclic stresses while exposed to the gasoline and its vapors as they would be in any commercial size storage tank.

Under the assumption of a weekly turnover for a large commercial tank operation, which is more frequent than normal in industrial practice, each week of operation for the demonstration unit is approximately equivalent to one and a half years of commercial tank operation. (Ten hours per day for five days per week in the demo-unit operation will subject the liners to approximately 80 cycles).

The demonstration unit will now be described in detail with the aid of Fig. 1 and Fig. 2. The tanks T1 and T2 were built out of 0.476 cm (3/16") thick steel plate. They are vertical cylinders with an open top and a dished bottom, measuring 1.83 m (6') in diameter by 1.83 m (6 feet) between tangent lines, supported on three I beam legs, equally spaced along their lower periphery. The top rim stands at 3.35 m (11') from the floor. Two sight levels covering a span of 33 cm (13") each, with the center of the sight tubes located approximately at the lower and upper operating liquid levels are provided in each tank. Tank T2 carries two float-type level controls LC1 and LC2 located at about the same level as the sight glasses. Block valves B1, B2, B3 and B4 permit isolation of the level controls from the tank's contents for maintenance and repair purposes. The differential between the controlled upper and lower liquid levels in the tank was set at 2.06 m (48").

Each tank carries a glass apparatus, G1 and G2. They are used for the determination of the gasoline loss and they are mounted in the tank's upper portions. Their assembly and operation will be described in detail in the section dealing with the gasoline loss determination. The circulating pump P, which delivers 178 dm^3/min (47gpm) is a vertical shaft centrifugal type,

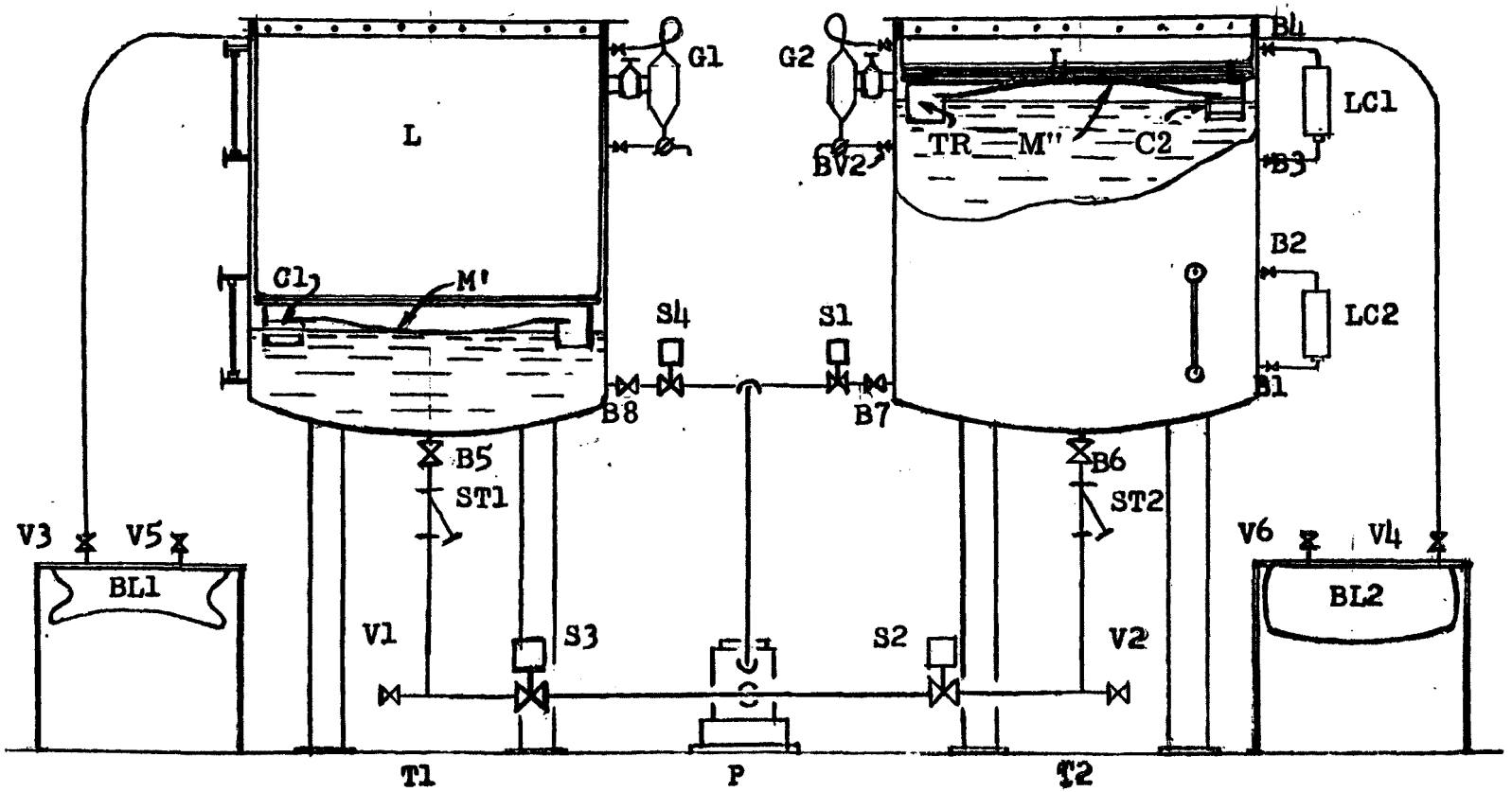

Figure 1. Schematic elevation view of pilot unit.

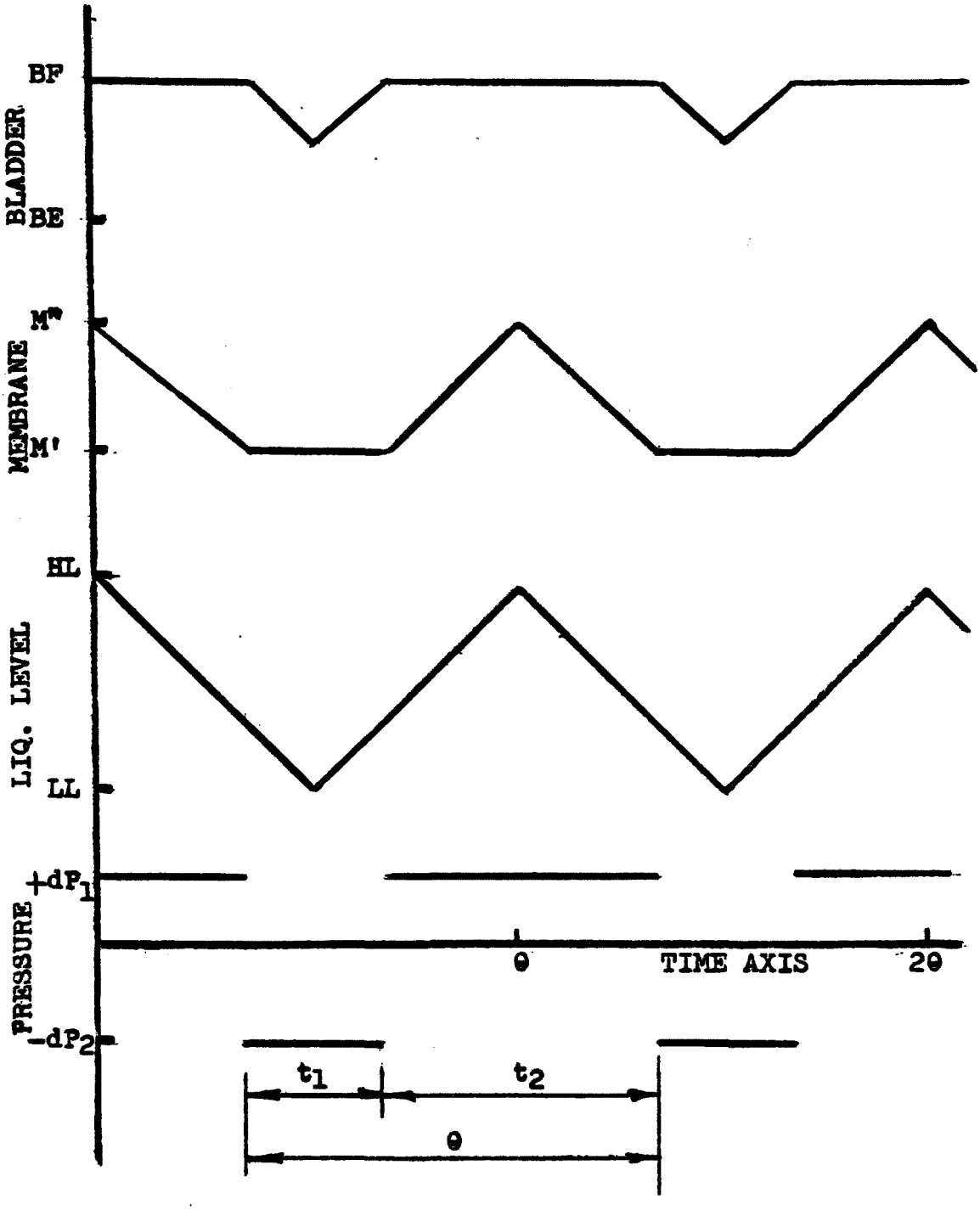

Figure 2. Time history of operational parameters.

totally enclosed and explosion-proof. Its suction and discharge ports are 2" IPS. Its suction port is connected to the tanks' bottom discharge nozzles and its discharge port to the tanks' side inlet nozzles. The block valves B5, B6, B7, and B8 permit isolation of the pump and its associate piping from the tanks.

Strainers ST1 and ST2 are provided in the suction lines to protect the pump and the solenoid valves from rust, scale, and occasional debris that may accumulate at the bottom of the tanks.

Solenoid valves S1 and S3 are of the normally open type (they close when energized) and the valves S2 and S4 are of the normally closed type (open when energized).

During the operation of the system, the transfer pump is kept always running. When liquid is being transferred from T2, into T1, valves S2 and S4 are open and valves S1 and S3 are closed. As soon as the liquid level in tank T2 reaches the low level, valves S2 and S4 are closed and valves S1 and S3 become open. Liquid now flows from tank T1 into T2. The automatic operation just described is achieved by the proper electrical interlock between the level controls and the solenoid valves. Manual switches are also provided to override the automatic control when so required.

Valves V1 and V2 are provided for the filling and the draining of the tanks.

A circular trough TR, whose cross section is depicted in Fig. 1, floats on the surface of the liquid. It is built of 0.3175 cm (1/8") thick steel plate, with its outside diameter measuring about 2.5 cm (1") less than the tank's inside diameter in order to avoid any undue friction or binding with the tank's shell at any point of its vertical displacement. The inside diameter of the trough is 1.47 m (58").

A circular membrane M, built out of a 0.0254 cm (10 mils) thick polypropylene sheet and having one of its sides coated with a 0.00254 cm (1 mil) thick film of an epoxy resin, is bolted to the internal rim of the circular trough. A neoprene gasket between the rim and the membrane is kept under compression by bolting a flat steel ring to the rim. This ring lays over the membrane's periphery and exerts an uniform pressure over the gasket.

A vertical liner L, affecting the shape of a cylinder with a diameter slightly smaller than the tank's inside diameter, is bolted to the upper portion of the shell and to the external rim of the floating trough. Here again, a neoprene gasket 0.3175 cm thick by 5 cm width, which is located between the liner and the shell, is kept under compression by segmental circular steel strips pressed against the liner by bolts. The sealing of the liner over the trough is done in an identical manner as described for the circular membrane M. The liner L is made from 0.0254 cm (10 mils) thick polyurethane coated on one of its sides with a 0.00254 cm thick film of an epoxy resin. The epoxy film, which provides most of the barrier

against the permeation of the gasoline vapors, faces the tank's shell. The height of the fully stretched liner is 1.83 m (6').

The vapor space between the liquid surface and the circular membrane M is kept in communication with the annular vapor space comprised between the shell and the liner L by the two conduits C1 and C2. These conduits are built out of two short lengths of 2" pipe (about 15 cm long each) that traverse the cross section of the trough and are welded to it at their ends.

In order to avoid corrosion of the tanks and troughs, they were coated with an epoxy paint which has outstanding resistance to attack by gasoline.

The vapor phase always contains gasoline vapors in a concentration higher than the one corresponding to the upper flammability limit (about 8% by volume), and consequently the danger of fire or explosion is practically non-existing. Nevertheless, it was consided convenient (mainly from a corrosion viewpoint) to ground the tanks and all their associated piping. Also a jumper was provided between the circular trough and the tank. An aluminum rod of 2.5 m (8') long was driven into the soil and wired to the tanks, thus serving as an anodic protection.

An overhead hoist travelling over an I beam was provided at each tank to aid in the installation of the liners.

During the operation of the tanks, the floating circular trough, which follows the continuous change of the liquid level, induces the folding or unfolding of the vertical liner L. Consequently, the annular space between the liner and the tank's shell, which is filled with air and the vapors of gasoline at their prevailing vapor pressure, changes continuously in volume. It decreases in volume for a rise in the liquid level and viceversa. If these volume changes would remain uncontrolled they would tend to induce pressure changes in the vapor space. Pressure would tend to increase for a raise in the liquid level and to decrease in the reverse case. An increase in pressure will tend to "balloon-up" the liner with the consequence that its orderly folding would be impaired and it would not allow the full utilization of the storage tank capacity due to a restriction in the available travel of the floating trough. The partially folded and "ballooned" liner would make contact with the tank's roof before the liquid level could attain its maximum height. On the other hand, a decrease in pressure would tend to create a sizable vacuum in the vapor space with the consequence that the liner would be pushed and pressed against the shell by the atmospheric pressure. The frictional forces so developed might become large enough to hold the liner so firmly pressed against the shell that the floating trough literally hangs-up. This in turn may stretch the liner beyond its safe limit and produce its failure. All of the above problems are avoided by providing a variable capacity container properly connected to the vapor space.

The bladders BL fulfill this requirement. Each is built out of the same flexible material as the vertical liner, and is essentially a flat cylinder, with both ends closed; it collapes and expands when very small

pressure differentials are applied across its surface. Its enclosed volume, when fully expanded, is larger than the tank's annular vapor space volume. Although in industrial practice the bladders would be located inside the storage tank and attached to the tank's roof, in the present case, because the tanks are open top, the bladders are located outside the tanks. The top of each bladder is cemented to a 0.9144 m (3') diameter disc of plywood and hangs freely from it. The valves V3 and V4 permit isolation of the bladders' content from their respective tanks, whose vapor spaces are connected to the bladder by a 2.54 cm (1") I.D. vinyl flexible tubing. Valves V5 and V6 serve for bleeding of the bladders into the atmosphere, which is done when the tanks are initially charged with the gasoline layer. In any position of the freely hanging bladder, except for the totally expanded one, the weight of the hanging portion is balanced by the pressure differential between the atmospheric pressure and the pressure inside the bladder, which consequently is under a slight vacuum. This vacuum is of an order of 0.5 mm of water column for the presently used size and shape of bladders. Very slight imperfections in the sealing areas of liners may allow some air to leak in which will eventually collect in the bladders.

In order to help in the understanding of the mechanism of the leakage of air and its eventual expulsion from the vapor space back into the atmosphere, a sequential operation of a tank will now be described. Let us begin with the liquid level located at or near its lowest working level. Let us further assume that the tank is now starting to be filled after being kept at the low level for a substantial period of time, during which the bladder has reached its fully expanded position due to air leaking in. The rise in the liquid level will now tend to compress the gas contained in the annular vapor space. The gas, now unable to flow into the bladder which is completely filled, will flow from the annular space into the space comprised between the membrane M and the surface of the liquid. The membrane will displace upwards, from its initial position M' to a final position M", which is attained when practically all of the gas in the annulus has been transferred, which in turn occurs when the higher operating liquid level has been reached. The gas enclosed by the liners and the bladder is now under a slight pressure caused by the weight of the membrane M, which is held suspended by the gas pressure. For the membranes utilized in this project, the pressure exerted is on the order of 0.3 mm of water column. If the tank is kept for a substantial time without unloading, the pressure differential across the liners will eventually cause a leak-out of the gas contained under the membrane M. A withdrawal of liquid now will cause the gas contained in the bladder to flow into the annular space.

Let us now consider the case where the tank is being filled and emptied continuously, which constitutes the other extreme of the variety of possible operational modes. In this case, a steady state is obtained in which the mass rate of air leaking in is equal to the mass rate of air leaking out. The air leaking out is essentially saturated with the vapors of gasoline. At the steady state the gas bounded by the liners undergoes cyclic changes of pressure, with the period of the pressure cycles (time elapsed between two crests or two troughs of the pressure wave) equal to the period of the

liquid level. Fig. 2 shows the liquid level change between the high (HL) and the low (LL) levels and the pressure wave, both as a function of time. It also indicates the positions of the flexible membrane M, between its two extremes M' and M", and the expansion and contraction of the bladder, between its fully expanded and its fully empty positions: BF and BE. It may be noticed that all of them are periodic functions of time with the same period Θ.

The pressure wave is a step function and indicates that the gas which is under a slight pressure during a fraction of the period Θ, undergoes a sudden change in pressure to become under a slight vacuum for the remaining of the period Θ. This is an oversimplification which does not take place in practice, the change in pressure is gradual but is effected in a relatively short time span.

Leakage out occurs during over-pressurization of the gas by the weight of the membrane M, which takes place for all the positions of the membrane above its lowest one: M'. It may be noticed that the bladder remains at its fully expanded position during the over-pressurization periods. The bladder is then under the slight pressure exerted by the membrane M.

Leakage in takes place during the under-pressurization periods, which occurs when the bladder is ina partially contracted position and therefore under a slight vacuum. The membrane M is at lowest position, with its weight supported by its attachment to the trough TR. In the present case, where the pressure differential $-dP_2$ created by the bladder is larger, in absolute value, than the pressure differential $+dP_1$, the gas remains under a vacuum for a shorter time (t_1) than when under pressure (t_2). The ratio t_1/t_2 depends on the ratio dP_1/dP_2 of the pressure differential and on the partial pressure of the gasoline in the gas.

The most important consequence of all of the above is that a storage tank subjected to a continuous turnover will experience a leakage loss larger than the one at any other operating mode. This consequence is a simple reflection of the fact that under continuous cycling, a sizable fraction of the total operating time is under conditions when the air is leaking out.

In the majority of the commercial storage applications, the cycling time (or in other terms, the time expended in filling and emptying the tanks) is a relatively small fraction of the total time the product is kept under storage, and consequently the losses due to leakage will be a small fraction of the total loss. The total loss being the sum of the loss due to gas permeation through the liners and the loss due to vapor leakage.

In summary it should be mentioned that the losses found in the present demo-unit would thus represent the upper boundary of the expected losses in commercial applications.

The start-up operation of the demo-unit will now be described in detail.

The first step consisted of the filling of the tanks with the required volume of water. A flexible hose was connected between a water faucet and the valve V1, and with all the block valves closed except B5, the tank T1 was filled to its upper operating level, which was ascertained by viewing the upper sight glass tube. The valves V1 and B5 were then closed and the flexible hose reconnected to valve V2. Valve 4 was now open and tank T2 filled to its lower operating level, as indicated by its lower sight tube. During the filling of the tanks, the air contained therein was displaced through the bladders by keeping the valves V3, V4, V5 and V6 open. The gasoline was introduced into the tank by pouring it into the top opening of the glass apparatus G2, after removal of the vinyl tube, and by opening the ball valve BV2, care being taken to maintain the liquid level in the tank below this valve.

In order to minimize the effect of the solubility of gasoline in water on the determinations of gasoline losses, the water was presaturated with gasoline by introducing about 8 dm^3 (2 gallons) of the same into the tank T2 and operating the plant for 1 week. By measuring the content of the gasoline layer at consecutive time intervals, it was ascertained that no or very negligible amounts of gasoline were transferred into the water and consequently the system attained equilibrium.

Following the presaturation run, 37.85 dm^3 (10 gallons) of gasoline were added to each tank which provides two layers of gasoline about 2.54 cm (1") thick each. The plant was then run for about one month, and weekly gasoline losses were determined. After ascertaining that the losses were practically identical in both tanks, it was decided that a better utilization of the demo-unit could be made by testing different liner materials in one of the tanks while keeping the other unchanged.

Tank T1 was then fitted with a vertical liner made out of a 0.005 cm (2 mils) thick film of a fluoropolymer, and the unit was run for another two months. Then the liner was removed and a new vertical liner, built out of a laminate of 0.005 (2 mils) thick of the same fluoropolymer and a 0.015 cm (6 mils) thick polyethylene, was installed. This was run for the remaining three months of the demonstration phase of the program.

In summary, an epoxy coated polyurethane liner was run for five consecutive months and kept standing during the sixth month, undergoing approximately 1800 cycles (each cycle is equivalent to one tank turnover), a fluoropolymeric liner was run for two months through about 650 cycles, and finally, a laminated liner was run two months and kept standing during the following month, which coincided with the sixth month of the demonstration phase of the project.

SECTION IV

METHOD USED FOR VAPOR LOSSES DETERMINATION

The vapors of the stored gasoline escape from the space enclosed by the liners into the surrounding atmosphere by permeating across the flexible membranes and by leaking through fissures, due to imperfect sealing at the attachment areas to the floating trough and to the tank. Also, but very seldom, leakage occurs through pinholes or other imperfections in the liners, such as defective seals between the adjoining modular panels that constitute the finished liner.

While the loss due to permeation is a known and predictable quantity that depends on the particular material used in the liner construction, its thickness, and the nature and temperature of the stored liquid, the leakage loss is unpredictable and it will depend on the quality control of the materials, workmanship and inspection procedures for leakage detection. Inasmuch as the pressure differentials across the liners are of very small order, the absolute values for the leakage is usually relatively small. Leakage due to pressure differentials occur essentially during the filling and emptying phase of the storage tank operation. Because the time expended in filling and emptying commercial size storage tanks is usually a small fraction of the total time the liquid is kept under static storage, the influence of the leakage loss on the total loss is minimal, and the total loss is therefore controlled by the permeation loss. The pre-estimated loss (prior to the initiation of the present project) was on the order of a few liters (gallons) for a six month plant operation or about 0.4 dm^3 (0.1 gallon) per week. The determination of such a small loss when dealing with relatively large tanks, made it impractical to determine it with any precision by measuring the level differentials in the tank. The precision of level readings in the sight glasses is about $\pm$ 0.16 cm ($\pm$ 1/16") which represents in a 1.83 m (6') diameter tank $\pm$ 4.16 dm^3 ($\pm$ 1.1 gallons). Therefore this method would be unacceptable.

The method used in this project measures the volume decrease between successive determinations for a small area of the gasoline layer. The ratio of the small area to the total area in the tank covered by the layer is known, and it is relatively simple to translate the measured volume decrease into the tank layer loss for the period of time between two successive determinations.

Fig. 3 illustrates schematically the apparatus used for the vapor loss determinations. The glass decanter G, fabricated out of 0.635 cm (1/4") thick Pyrex glass, is supported by a clamp on a rod frame attached to the tank (not shown in the illustration). It has a side tube facing a 2" IPS steel nipple which is threaded into a bronze gate valve (GV). A polyurethane sleeve was tightly slid and clamped over the nipple and the side tube, assuring a leakproof connection. A three-way glass petcock P allows the flow of liquid between the tank and the decanter, in one case; the drainage of the decanter through the elbowed tubing, in another case; or the flow from the

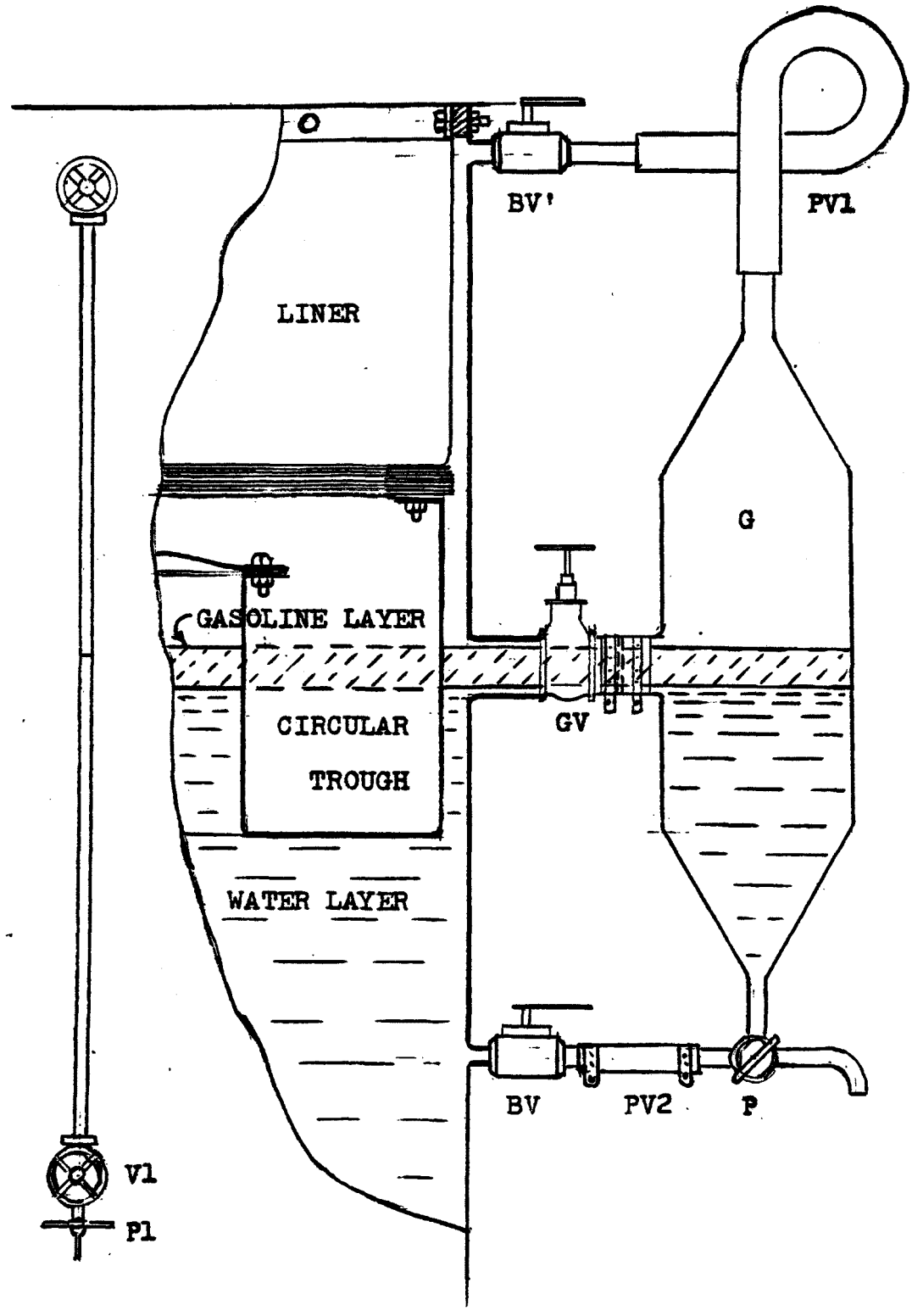

Figure 3. Vapor loss determination apparatus.

tank and through the elbowed tubing, in the third case. A polyvinyl tube PV2 provides a flexible connection between the decanter and the tank. The gas phases of the decanter and the tank are connected by a 2.54 cm ID polyvinyl tubing PV1.

In order to determine the volume of the gasoline layer held in the tank at any given time, a fraction of the layer is collected in the decanter and its volume determined. The knowledge of the ratio of the tank area to the decanter area permits the calculation of the total volume of gasoline contained in the tank's layer.

To obtain the establishment of a layer in the decanter with the same thickness as the tank's layer, it is necessary that the liquid level selected be such as to allow the flow of the gasoline from the tank into the decanter when the gate valve GV is open. This requirement implies that the gasoline layer should partially or totally fill the circular duct connecting the tank to the decanter.

The procedure followed for the volume determination consisted of the following steps:

1. At the start, the valves GV, BV and BV' are closed and the decanter G is empty.

2. A liquid level is set and marked on the glass tube of the sight gage, in compliance with the requirement that the gasoline layer should partially or totally fill the connecting duct.

3. The liquid level is now brought to an intermediate level which lays below the above mentioned set level but remains within the glass tube.

4. The gage's valve V1, which communicates it with the tank contents, is now closed and the contents of the glass tube are drained through the petcock P1. This will remove any slugs of gasoline that entered the tube while raising the liquid level.

5. P1 is closed and V1 is opened which allows the glass tube to be filled only with water.

6. The liquid level in the tank is now brought back to the set level by manually operating the pump's controls and observing the glass gage. This will insure that the gasoline-water interface is always at nearly the same level in all determinations. The liquid in the tank is left standing still overnight to insure that any gasoline droplets that may have been dispersed in the liquid phase will collect in the top layer.

7. With valve GV still closed, valves BV and BV' are now opened. Water from the tank fills the decanter until hydrostatic equilibrium is attained. Valve GV is then opened, allowing the gasoline from the tank's layer to flow into the decanter. After a period of two hours, which has proven ample for

attainment of equilibrium, valves BV and GV are closed. The decanter now contains a gasoline layer of exactly the same thickness as the one in the tank.

8. The water layer in the decanter is slowly decanted off into a beaker by manipulating the three-way petcock. Decantation proceeds until the gasoline layer reaches the petcock, care being taken to leave a small water column between the petcock and the gasoline.

9. The gasoline layer is drained off the decanter into a beaker together with the small amount of water that remained in the three-way petcock and the 90° glass tube.

10. The collected gasoline is poured into a burette, where the accompanying water that settles at the bottom is drained off. The remaining gasoline is measured and recorded. The burettes used in these determinations could be read to 0.2 cm^3.

The area covered by the gasoline layer collected in the decanter was calculated by measuring the height of the layer and its volume. It was found to be 160 cm^2. The area covered by the gasoline and occupying the tank's available internal cross section was found to be 18,600 cm^2. The ratio of the tank area to the decanter area is therefore 18,600/160 = 116.

There are two systematic errors associated with the above described volume determinations. One error is caused by the lack of coincidence of the liquid level with the mark set in the glass tube. The smallest division in the glass tube is 0.16 cm (1/16") and consequently the liquid level can only be read within ± 0.16 cm of the set mark. Consequently, the gasoline layer that collects in the decanter during step 7 of the determination procedure may be located within 0.16 cm above or below its assumed position. This uncertainty in the location in turn causes an uncertainty in the volume of the portion of the layer comprised within the connecting circular duct, because of the variation of the layer's cross-section with its elevation within the duct. From the dimensions of the duct and the thickness of the gasoline layer, it has been calculated that the maximum error to be expected from this source at each volume determination is ± 0.65 cm^3. The other error is due to the readings of the volume of gasoline in the measuring burette. The burette utilized had a capacity of 100 cm^3, and the volume collected in the decanters were of the order of 300 cm^3. Three readings were thus required which introduced an error of ± 0.6 cm^3 per determination. The total systematic error is thus equal to or less than ± 1.25 cm^3 per determination.

The gasoline loss experienced in the tank between two successive determinations is calculated as follows:

First define:

V_i = the gasoline volume in the decanter determined at test No. i

V_{i+1} = the gasoline volume in the decanter determined at test No. i+1

dV_D = the loss of gasoline in the decanter

dV_T = the loss of gasoline in the tank

116 = the ratio between the areas covered by the layers in the tank and in the decanter.

We have then:

$$dV_D = V_i - V_{i+1} \pm 2.5 \text{ cm}^3 \tag{4-1}$$

$$dV_T = 116.\ dV_D - V_i \pm 291.25 \text{ cm}^3 \tag{4-2}$$

The volume collected in the decanter is discarded, since it is not an operating loss, it has to be substracted from the actual loss.

When the gasoline loss is desired to be found between determinations i and i + n, equations 4-1 and 4-2 become:

$$dV_D = V_i - V_{i+n} \pm 2.5 \text{ cm}^3 \tag{4-3}$$

$$dV_T = 116.\ dV_D - \sum_{i}^{i+n-1} V_i \pm (290 + 1.25\ (n-1)) \tag{4-4}$$

SECTION V

RESULTS OF THE VAPOR LOSS DETERMINATIONS

GENERAL

Table 5-1 contains the data obtained for the six months operation of tank No. 2. As described in Section III, tank No. 2 was fitted with an epoxy coated polyurethane liner. This liner was continuously operated for 5 months at an average of 10 hours per day and 5 days per week. It was thus subjected to about 1800 cycles. During the sixth month, the system was left standing still to determine the static storage loss.

Table 5-2 contains the data for the presaturation run.

Table 5-3 contains the data obtained for the fluoropolymeric liner that was fitted in tank 1 and operated for 2 months continuously. Only 2 sets of data were taken in the last 5 weeks of operation.

Table 5-4 contains the data obtained for the liner built out of a laminate of a 0.005 cm thick film of a fluoropolymer and a 0.015 cm thick polyethylene film, which was fitted in the tank 1. The liner was run continuously for 2 months and kept standing still for the 3rd month.

A plot of the cumulative loss against time for the tank No. 2 is represented in Fig. 4. The curve shown was calculated from the data in the table 5-1, by the least squares method. The curve has a sharp change of slope that occurs at the beginning of the sixth month of operation, coinciding with the change in the operation regime, i.e. from dynamic to static. Fig. 5 represents a similar plot for the data shown in table 5-4.

DYNAMIC LOSS RATE FOR TANK No. 2

From table 5-1, the total loss of gasoline during the 5 months period of continuous operation (dynamic storage condition) is calculated as follows:

Volume decrease in the decanter between the determination No. 20 and No. 0 :

$$dV_D = 347.6 - 251.8 = 95.8 \text{ cm}^3 \qquad (5\text{-}1)$$

The sum of the volumes of gasoline collected in the decanter and discarded from the twenty determinations is:

$$\sum_{i=0}^{19} V_i = 6068.8 \text{ cm}^3 \qquad (5\text{-}2)$$

Applying the formula (4-4) gives:

$$dV_T = 116.\ dV_D - \sum V_i \pm (116 \times 2.5 + 1.25 \times 19) \text{ cm}^3 \qquad (5\text{-}3)$$

Table 5-1. VAPOR LOSS DETERMINATIONS AT TANK No. 2

Date, 1978	Determination number, i	V_i Volume of gasoline collected in the decanter, cm^3	dV_D Loss at decanter, cm^3	dV_T Loss at tank, cm^3	Cumulative loss at tank, cm^3
6/29	0	347.6			
7/7	1	341.0	6.6	417	417
7/14	2	338.4	2.6	-40	377
7/21	3	333.6	4.8	219	596
7/28	4	327.0	6.6	431	1027
8/4	5	324.2	2.8	-2	1025
8/11	6	318.8	5.4	308	1328
8/18	7	312.2	6.6	447	1775
8/25	8	310.4	1.8	-103	1672
9/1	9	305.2	5.2	293	1965
9/8	10	299.6	5.6	344	2309
9/15	11	298.4	1.2	-160	2149
9/22	12	295.6	2.8	26	2175
9/29	13	288.8	6.8	493	2668
10/6	14	284.2	4.6	245	2913
10/13	15	278.8	5.4	342	3255
10/20	16	272.4	6.4	464	3719
10/27	17	270.4	2.0	-41	3678
11/3	18	265.2	5.2	333	4011
11/17	19	257.0	8.2	686	4697
12/1	20	251.8	5.2	346	5043
12/15	21	250.0	1.8	-43	5000
12/29	22	246.4	3.6	168	5168

Table 5-2. PRESATURATION RUN

Date, 1978	Determination number, i	V_i Volume of gasoline collected in the decanter, cm^3	dV_D Loss at decanter, cm^3	Gasoline transferred to water, cm^3
6/22	1	64.8		
6/26	2	51.4	13.4	1589.6
6/28	3	50.8	0.6	18.2

Table 5-3. VAPOR LOSS DETERMINATIONS AT TANK No.1
Fluoropolymeric liner

Date, 1978	Determination number, i	V_i Volume of gasoline collected in the decanter, cm^3	dV_D Loss at decanter, cm^3	dV_T Loss at tank, cm^3	Cumulative loss at tank, cm^3
8/25	0	273.2			
9/29	1	258.4	14.8	1443	1443

Table 5-4. VAPOR LOSS DETERMINATIONS AT TANK No. 1
Laminated Liner

Date, 1978	Determination number, i	V_i Volume of gasoline collected in the decanter, cm^3	dV_D Loss at decanter, cm^3	dV_T Loss at tank, cm^3	Cumulative loss at tank, cm^3
10/6	0	306.6			
11/3	1	295.8	10.8	946	946
12/1	2	287.4	8.4	678	1624
12/15	3	284.8	2.6	14	1638
12/29	4	282.2	2.6	17	1655

$$dV_T = 116 \times 95.8 - 6068.8 \pm 314 = 5044 \pm 314 \text{ cm}^3 \qquad (5\text{-}4)$$

The relative error (e_r) attached to dV_T is:

$$e_r = \frac{314 \times 100}{5044} = 6.3\% \qquad (5\text{-}5)$$

The yearly loss rate (L_y) is then:

$$L_y = dV_T \times \frac{12 \text{ mo.}}{5 \text{ mo.}} = 12106 \ \frac{\text{cm}^3}{\text{year}} \ \left(3.2 \ \frac{\text{gallons}}{\text{year}}\right) \qquad (5\text{-}6)$$

with a precision of ± 6.3%

STATIC LOSS RATE FOR TANK No. 2

The loss experienced in tank No. 2 at standstill (static storage condition) is calculated from determination Nos. 20, 21, and 22. Using the procedure just outlined, we obtain:

$$dV_D = 251.8 - 246.4 = 5.4 \ \text{cm}^3 \qquad (5\text{-}7)$$

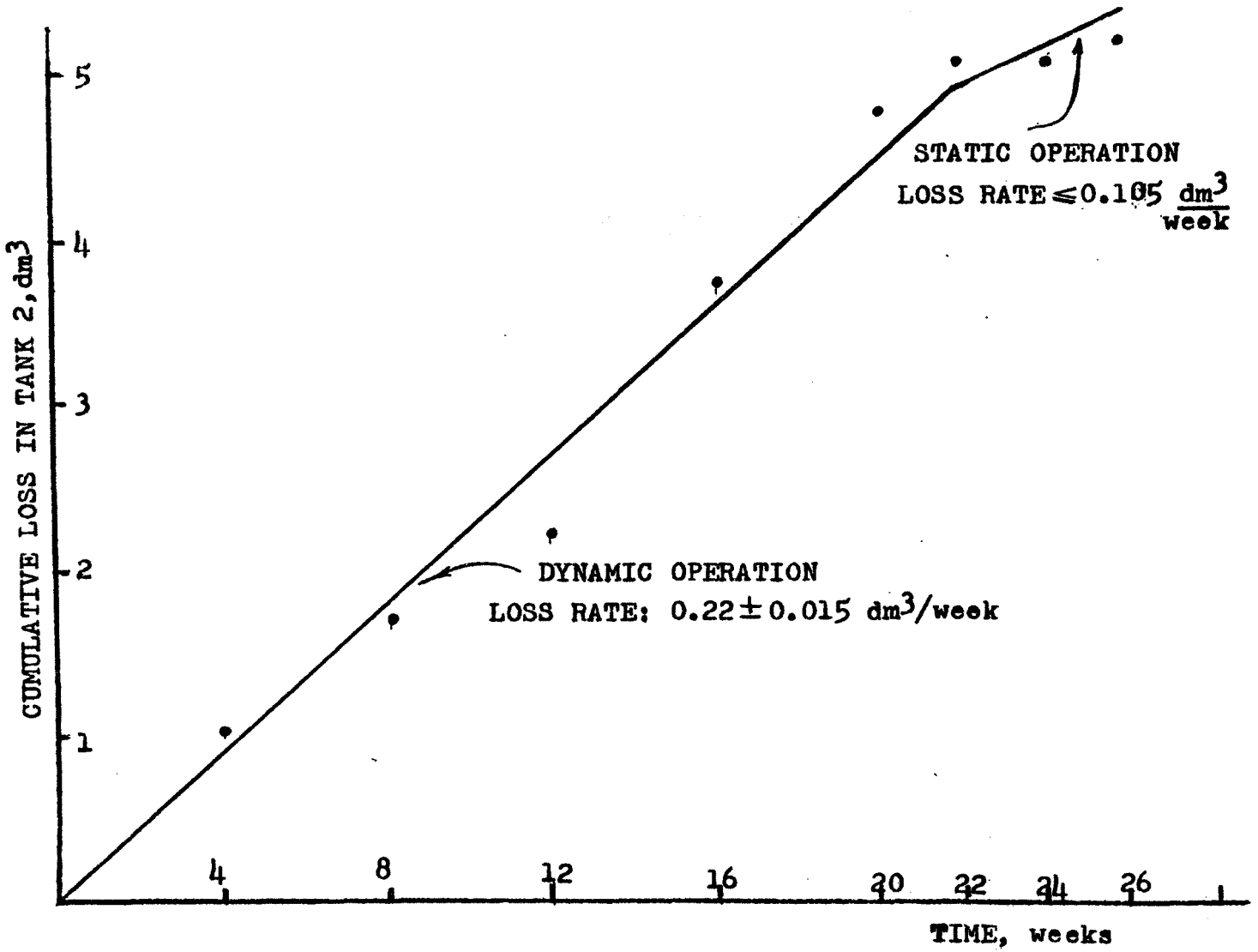

Figure 4. Loss rate for tank 2.

$$\sum_{i=20}^{21} V_i = 251.8 + 250 = 501.8 \quad cm^3 \tag{5-8}$$

$$dV_T = 116 \times 5.4 - 501.8 \pm (116 \times 2.5 + 1.25 \times 2) \ cm^3 \tag{5-9}$$

$$dV_T = 124.6 \pm 295 \quad cm^3 \tag{5-10}$$

dV_T is thus comprised between -170 cm^3 and +420 cm^3. The negative number would indicate a gain in the system, which is absurd and therefore discarded. The positive number indicates that the loss is between zero and 420 cm^3. The yearly loss rate is then equal or less than:

$$L_y \leqslant 420 \times 12 \text{ mo.} = 5040 \ \frac{cm^3}{year} \quad (1.33 \ \frac{gal}{year}) \tag{5-11}$$

If it is assumed for the moment that this loss rate is due to gas permeation through the liners, which have a total surface of 12.54 m^2 (135 ft^2), then the permeation coefficient (C_p) should be equal or less than:

$$C_p \leqslant \frac{5040}{365 \times 18.54} = 1.1 \ \frac{cm^3}{day.m^2} \text{ or } 0.77 \ \frac{g}{day.m^2} \tag{5-12}$$

Permeation determinations carried out by the pouch method (i.e., in pouches fabricated with the same material as the liner) indicated a coefficient of 0.53 $g/day.m^2$.

It may then be concluded than during static storage conditions the loss rate is essentially due to the gas permeation through the liners. The larger loss rate found for dynamic storage conditions is attributed to leakage in addition to permeation as explained in Section III.

SCALE-UP OF LOSS RATES TO COMMERCIAL SIZE TANKS

In order to calculate the emission control efficiencies obtainable with the present technology when applied to commercial size tanks, a tank measuring 100 ft. in diameter and 40 ft. in height is considered. The loss rate for a tank of any size is here assumed to be proportional to the area of the liners fitted into the tank. This area is the sum of the cross-sectional and lateral areas of the tank. For the size mentioned above, the total lined area measures 1897 m^2 (20,420 ft^2). The ratio of the areas of the commercial tank to the demo-unit tank is 1897/12.54 = 152. The yearly loss (LD_y) for the commercial tank operating under dynamic storage condition would then be:

$$LD_y = 12.106 \ dm^3/year \times 152 = 1840 \ dm^3/year \ (11 \text{ Bbls/year}) \tag{5-13}$$

The static storage yearly loss is equal or less than:

$$LS_y \leqslant 5.04 \ dm^3/year \times 152 = 766 \ dm^3/year \ (4.8 \text{ Bbls/year}) \tag{5-14}$$

In summary, 100' Ø x 40' H storage tank holding gasoline and fitted with an epoxy coated polyurethane liner is expected not to emit more than 11 Bbls/year under dynamic storage and 5 Bbls/year under static storage conditions.

DYNAMIC LOSS RATE FOR TANK No. 1

The loss rates experienced in tank No. 1 when fitted with the laminated liner are calculated from the data in table 5-4. For the loss during dynamic storage condition we have: (determinations 0, 1 and 2).

$$dV_D = 306.6 - 287.4 = 19.2 \text{ cm}^3 \tag{5-15}$$

$$\sum_{i=0}^{1} V_i = 306.6 + 295.8 = 602.4 \text{ cm}^3 \tag{5-16}$$

$$dV_T = 19.2 \times 116 - 602.4 \pm (116 \times 2.5 + 1.25 \times 2) \text{ cm}^3 \tag{5-17}$$

$$dV_T = 1625 \pm 295 \text{ cm}^3 \tag{5-18}$$

The yearly loss rate is:

$$LD_y = 1625 \times \frac{52 \text{ weeks}}{8 \text{ weeks}} = 10562 \frac{\text{cm}^3}{\text{year}} \text{ or } 2.8 \frac{\text{gal}}{\text{year}} \tag{5-19}$$

with a precision of ± 18%.

STATIC LOSS RATE FOR TANK No. 1

For the loss rate under static storage conditions we have from determinations 2, 3 and 4:

$$dV_D = 287.4 - 282.2 = 5.2 \text{ cm}^3 \tag{5-20}$$

$$\sum_{i=2}^{3} V_i = 287.4 + 284.8 = 572.2 \text{ cm}^3 \tag{5-21}$$

$$dV_T = 5.2 \times 116 - 572.2 \pm 295 \text{ cm}^3 = 31 \pm 295 \text{ cm}^3 \tag{5-22}$$

The loss will thus be between -264 cm^3 and + 326 cm^3. The negative number indicates a gain in the system, which is absurd and is therefore discarded. The loss will thus be between zero and + 326 cm^3. The maximum yearly rate loss to be expected is then:

$$LS_y \leqslant 326 \times 12 \text{ mo.} = 3912 \frac{\text{cm}^3}{\text{year}} \left(1 \frac{\text{gal}}{\text{year}}\right) \tag{5-23}$$

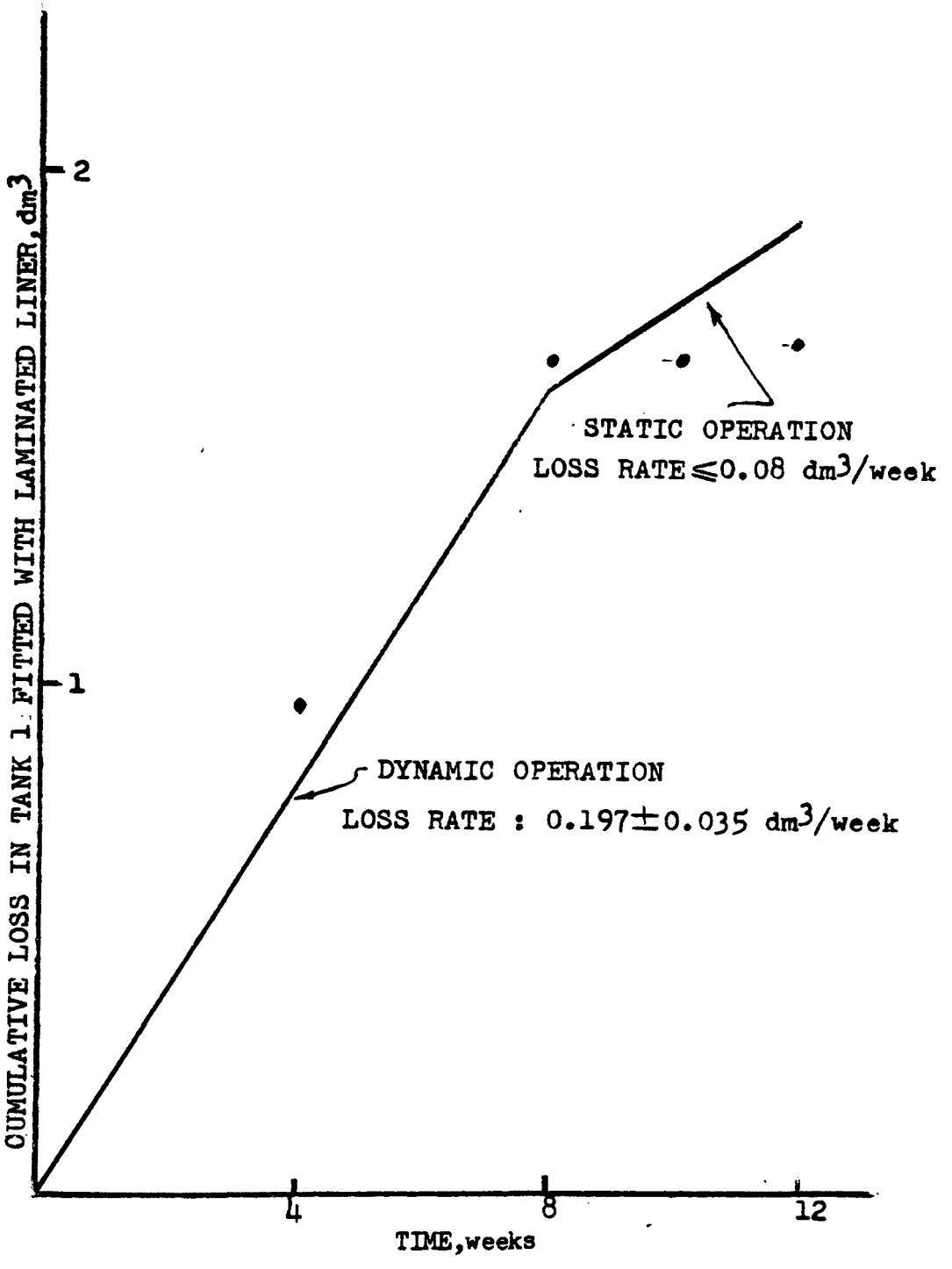

Figure 5. Loss rate for tank 1.(Laminated liner)

The maximum gas permeation coefficient to be expected would be:

$$C_p = \frac{3912}{365 \times 12.54} = 0.85 \ \frac{cm^3}{day.m^2} \text{ or } 0.6 \ \frac{g}{day.m^2}$$

Gas permeation tests conducted with a material identical to the one of the liner, indicated a zero permeation loss. The pouch method was also used here. It can be concluded that the loss rate for this type of liner is essentially nil under static storage conditions, within experimental error.

The sharp change in the rates when passing from dynamic to static storage conditions, clearly indicate that the mechanism of loss is quite different in each regime. As mentioned previously, the higher rate obtained for dynamic conditions is due to additional losses by leakage through imperfections in the seals or other portions of the liners. This leakage is caused by pressure differentials created across the liners, as explained in detail in Section III of this report.

SECTION VI

ACCURACY OF THE DATA AND THE RESULTS

It was shown in Section IV that each data point (i.e., each determination of the volume of gasoline collected in the decanter) was affected with a possible error of $\pm$ 1.25 cm^3. It was also shown that the probable error associated with the calculation of the gasoline loss in the tank between any two determinations was:

$$e_T \leqslant (116 \times 2.5 + 1.25\ (n-1))\ cm^3 \qquad (6\text{-}1)$$

where:

e_T is the error attached to the calculated value of the gasoline loss between the determinations numbered i and i + n

The error committed increases very slowly with the number n, while the calculated loss in the tank increases very nearly proportionally with the number n. Consequently, the relative error of the calculated value dV_T (volume lost between the two determinations) decreases very rapidly with n. The relative error e_r is defined as:

$$e_r = \frac{e_T}{dV_T} \qquad (6\text{-}2)$$

where: e_r is the relative error

e_T is the absolute error

dV_T is the loss of gasoline in the tank between determinations. The error e_T is of the order of 300 cm^3.

In order to obtain a relative error e_r less than 10%, dV_T should be larger than 3000 cm^3. This requirement was fulfilled in tank No. 2 where the total calculated loss was close to 5000 cm^3 for the dynamic storage operation. The accuracy of the loss found for the tank No. 1 when fitted with the 2 mils thick fluropolymeric liner and operating under dynamic storage conditions is:

$$dV_T = 1443\ cm^3/\text{month or } 4.6\ \text{gal/year} \qquad (6\text{-}3)$$

$$e_T \leqslant 292\ cm^3 \qquad (6\text{-}4)$$

$$e_r \leqslant \pm\ 20\% \qquad (6\text{-}5)$$

This low precision is due to the short time span between determinations and to the low loss rate. For the tank No. 1 when fitted with the laminated liner and for dynamic storage operation the accuracy was found to be $\pm$ 18%. (See Section V, formula 5-18).

SECTION VII

INTERPRETATION OF THE RESULTS OBTAINED

The results obtained for the emission rates of gasoline in the demo-unit can be compared with emission rates from commercial size uncontrolled storage tanks. The correlations and formulas established by the American Petroleum Institute have been determined from data obtained on commercial size tank operations. In order to establish a comparison on the same basis, the results from the demo-unit will be scaled-up to commercial size tanks. The scale-up factor is assumed to be proportional to the area of the liners. The justification for this assumption rests on the fact that vapor permeation losses are proportional to the area of the permeating membrane. Although it would seem more justifiable to use a ratio of the lengths of the sealing surfaces of the liners for the leakage losses, the use of the areas ratio will provide a more conservative approach. This latter ratio is the square of the former one.

We will now consider the scaled-up results obtained from the 3 different types of liners utilized in the demo-unit and compare them with the data obtained from the API correlations for an uncontrolled commercial sized tank. A commercial tank measuring 30.48 m (100') in diameter by 12.2 m (40') in the height will be considered for comparison purposes. The scale-up factor between this size tank and the demo-unit tank size is 152.

EXPECTED CONTROL EFFICIENCIES

Polyurethane-Epoxy Coated Liner In Tank No. 2

Dynamic Storage Condition-

The dynamic rate loss for the demo-unit size found at (5-6) was 12.1 dm^3/year and the scale-up dynamic loss rate (LD_y) is:

$$LD_y = 12.1 \times 152 = 1840\ dm^3/\text{year or } 11\ \frac{\text{Bbls}}{\text{year}}$$

Number of cycles undergone by the liner: 1800

The loss rate for the uncontrolled commercial size tank is found from Fig. 12 in API Bulletin 2518*. For a gasoline having a vapor pressure of 3516 Pa (5 psia) the loss is: 1,589,700 dm^3/year (10,000 Bbls/year). The emission control efficiency (EFF) thus provided by the Stop-Los Company new technology is then:

$$EFF = 100 \times (1 - 11/10{,}000) = 99.9\% \qquad (7\text{-}1)$$

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* American Petroleum Institute, Evaporation loss from fixed-roof tanks, API bulletin 2518, June 1962.

The maximum number of cycles or turnovers listed in this nomograph is 400/year.

Static Storage Condition-

The scaled-up static loss rate (LS_y) for the demo-unit was found at (5-14) to be:

$$LS_y \leqslant 766 \text{ dm}^3\text{/year } (4.8 \text{ Bbl/year})$$

The equivalent of static storage is found in the API Bulletin 2518 under "Breathing Loss". Breathing losses are a function of the average daily temperature change, the tank outage, the vapor pressure of the gasoline and the tank diameter, and a paint factor, which is assumed, conservatively, to be 1. The average daily temperature change will be taken for the same geographical area where the demo-unit is located. The choice of the tank outage is somehow arbitrary, a tank about 2/3 full will be here considered. The average daily temperature change in the Newark, N.J. area is 8.33 K (15°F), the tank outage: 4.27 m (14'), the gasoline vapor pressure: 3516 Pa (5 psia). From Fig. 8 of API Bulletin 2518:

$$\text{Breathing loss} = 95382 \text{ dm}^3\text{/year } (600 \text{ Bbls/year})$$

The emission control efficiency provided by the Stop-Los Company technology is then:

$$EFF \geqslant 100\ (1 - 766/95382) = 99.2\% \qquad (7\text{-}2)$$

Polyethylene-Fluoropolymer Laminate Liner In Tank No. 1

Dynamic Storage Condition-

The value found at (5-19) for the demo-unit was:

$$LD_y = 10.562 \text{ dm}^3\text{/year}$$

Scaling-up this value we obtain:

$$LD_y = 10.562 \times 152 = 1605 \text{ dm}^3\text{/year or } 10 \text{ Bbl/year}$$

Number of cycles undergone by the liner: 700

The loss rate for the uncontrolled commercial size tank is the same as found above, or:

$$\text{Loss} = 1{,}589{,}700 \text{ dm}^3\text{/year } (10{,}000 \text{ Bbl/year})$$

The emission control efficiency is then:

$$EFF = 100\ (1 - 10/10{,}000) = 99.9\%$$

Polyethylene-Fluoropolymer Laminate Liner in Tank No. 1
Static Storage Condition-

It was shown before that the loss rate was essentially nil and consequently it should provide a control emission efficiency of nearly 100%.

SECTION VIII

LIFE EXPECTANCY OF LINERS

It is known that the liners' materials of construction are essentially inert to attack by the stored gasoline and similar hydrocarbons such as crude oil, kerosene, jet fuel, etc., when they are in a stress free state. The effect of the application of repetitive alternating stresses, such as the ones developed during the folding and unfolding of the vertical liners are also known for the cases where the environment surrounding the liners is atmospheric air. Folding endurance tests which are routinely performed and reported* indicate that the materials will withstand a large number of alternating stresses before failing. For instance, polyurethane has virtually infinite folding endurance; polyethylene can endure about 100,000 cycles before failing and the fluoropolymer utilized in the laminated liner will withstand about 250,000 cycles. But, the endurance of these materials when cyclicly stresses in an atmosphere containing hydrocarbon vapors was not known with certainty prior to the initiation of the present program.

The constancy of the loss rate throughout time, as shown by the slopes of the curves plotted in Figures 4 and 5, would indicate that no cracks or other types of mechanical failures were sustained by the liners. The inspection of the liners during and after the completion of the test periods tends to corroborate this assumption.

In a survey of oil companies conducted by the API (API Bulletin 2518, page 19), it was found that the great majority of storage tanks had a yearly turnover of 10 or less. This implies that on the average, a storage tank is filled and emptied once every 5 weeks. Yearly turnovers of the order of 30 to 40 were infrequently found. In this report a weekly turnover was assumed for a commercial type operation.

The liners used in the demo-unit underwent between 700 to 1800 cycles, each cycle corresponding to a tank turnover. The minimum life expectancy would then be in the order of 14 years for the laminated liner, and about 34 years for the polyurethane liner. It may then be concluded that under normal operating conditions the liners should render satisfactory service for a 20 years period, which would be an acceptable standard to the industry.

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* McGraw Hill, Modern Plastics Encyclopedia, 1974-75, Pages 730, 732

SECTION IX

ECONOMICS

An economic comparison between the new technology dealt with in this report and the conventional technology for emissions control of stored petroleum and its derivatives, clearly shows the new technology to be highly competitive.

The yardstick used in this comparison is the installed cost of the devices offered by both technologies. Installed costs for the new technology were extracted from recent quotations made by the Stop-Los Company to prospective customers. The installed costs for the conventional technology were estimated from the figure 8-5 of the Petroleum Processing Handbook*.

Because the data in this reference are for the years 1964-1965, an escalation factor of 2 was used to arrive at present day costs. The escalation factor was taken from the Business Week Magazine's Index **: Consumer Price Index/BLS. The datum (100) of this Index is for the year 1967. For January 1979 the Index stood at 204.7.

The installed cost for the conventional devices, i.e., double deck and pontoon types of floating roofs, as well as for the devices of the new technology, are plotted against tank capacities in figure 6.

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* William F. Bland, Robert L. Davidson. Petroleum Processing Handbook, McGraw Hill Book Co., 1967, page 8-24.

** Business Week, McGraw Hill Inc., March 12, 1979, page 2.

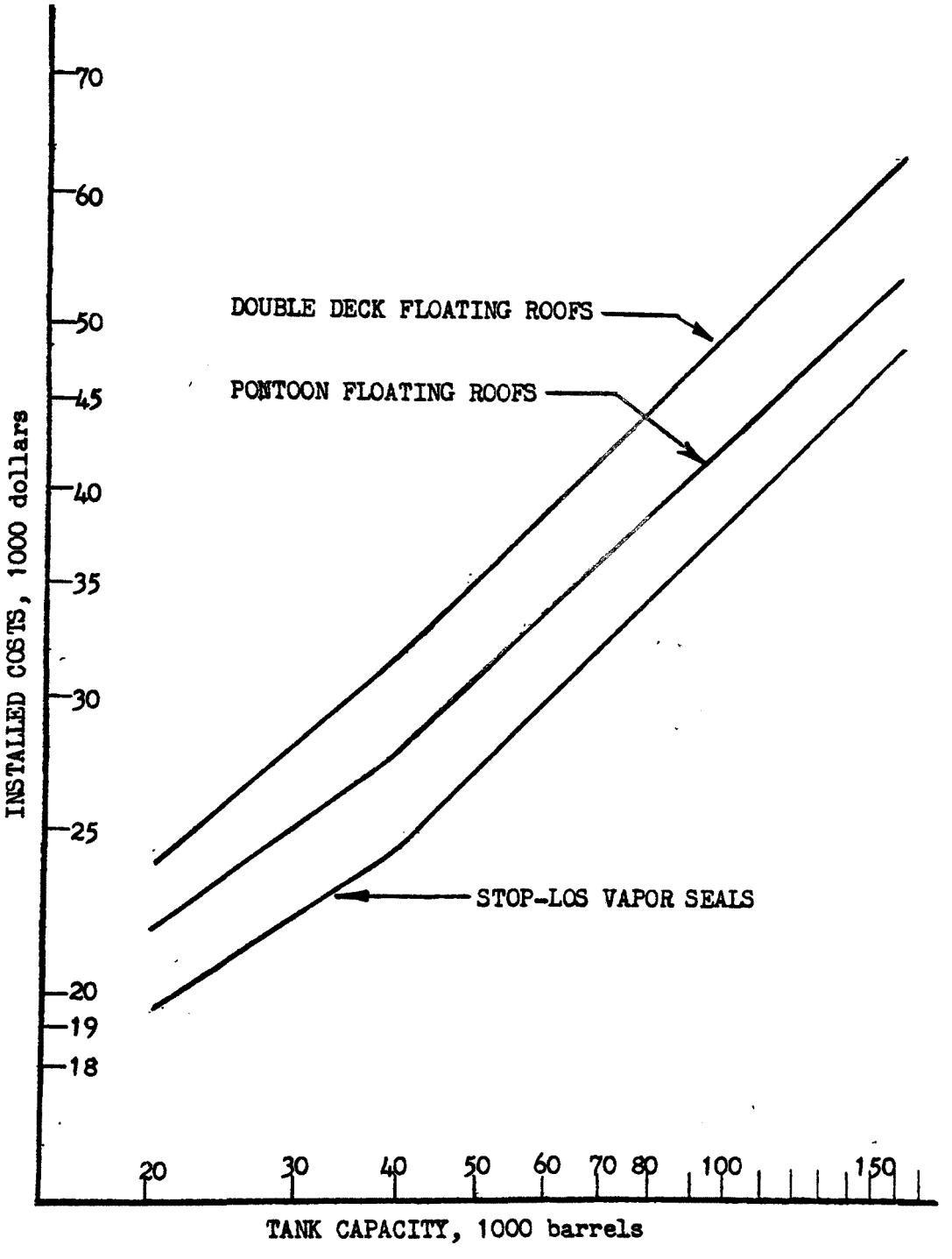

Figure 6. New and old technologies cost comparison.

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT The report gives results of a project to determine the technical and economic feasibility of using flexible plastic membranes to control emissions from gasoline storage tanks. The emission rates and the expected life of the membranes were to be established. A demonstration pilot unit was built and operated. The emission rates were determined, as well as the life expectancy of the membranes. The results indicate that emission control of 99-plus percent, compared to uncontrolled tanks, can be achieved readily, and that the life expectancy of the membranes is in the order of 20 years of continuous service. The estimated installed cost of these devices for commercial application is very competitive with conventionally used floating roofs.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Air Pollution Control	13B
Gasoline	Stationary Sources	21D
Storage Tanks	Flexible Plastic Membranes	13D
Emission		14B
Membranes		11G
Plastics		11I

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