THE USE OF ACTIVATED CARBON ADSORPTION FOR VINYL CHLORIDE EMISSION REDUCTION

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INTRODUCTION

The emergence in 1974 of vinyl chloride as apparently related to deaths due to hemangiosarcoma of the liver in a number of PVC workers focused attention on the control of emissions of this chlorinated hydrocarbon into the environment.

Conventional recovery systems in PVC plants have not effected complete and economical separation of vinyl chloride from inert gases which are introduced into the polymerization process. Purges of these inert gases from various phases of the process contain vinyl chloride and, as they are normally vented to the air, constitute a concern.

Tenneco Chemicals has developed a unique carbon adsorption technology to reduce vinyl chloride emissions from various phases of the PVC manufacturing process. The first successful commercial-scale application of this technology was at Tenneco's Pasadena, Texas PVC manufacturing plant where a carbon adsorption unit was installed in early 1975. Over the past twelve months, it has demonstrated that the VCM content of emissions to the environment from the sources treated can be consistently reduced to levels below 10 parts per million. The use of the process, therefore, appears of value in meeting some phases of the EPA requirements as contained in that Agency's recent proposed Regulations.[7]

THE STATE OF THE ART

There are several known methods for removal of VCM from gas streams emitted from the PVC polymerization process, but each has its disadvantages. Some of these are:

1. Scrubbing of inert gas streams containing VCM is a reliable, but generally uneconomical means of removing VCM. Because of the solubility characteristics of VCM in most applicable solvents, cooling of the gases below 0°C is required. Also, to keep equipment size down, solvent systems are generally operated under pressure which adds to the process complexity.[6]

2. Combustion of the gas stream to oxidize VCM to carbon dioxide, water and hydrochloric acid followed by caustic scrubbing of the off-gas to remove hydrochloric acid is being practiced commercially on a limited scale. However, the high cost of the required equipment and fuel make this approach undesirable.

3. The development of an oxyphotolysis route to the destruction of VCM has been reported, but its technical and economic feasibility remains as yet unproven.

4. The use of refrigerated vent condensors is applicable only where the concentration of the inerts in the gas stream treated is low. The energy requirement to cool the gas stream to -29°C is high, and the treated inert gases still contain a high amount of vinyl chloride.[5]

Since the above methods were generally undesirable, or uneconomic, Tenneco embarked on a development program in 1973 utilizing activated carbon. The utilization of various forms of carbon as adsorbents has a long history. Centuries ago, Hindus filtered water through charcoal and the purification of sugar solutions with carboneous materials was carried out as early as the thirteenth century. In the latter part of that same century, Scheele found that carbon had the ability to adsorb gases, and since then, carbon adsorbents have found wide application in industry.[9]

SOURCES OF VINYL CHLORIDE EMISSIONS

Some sources of VCM emissions in the manufacture of PVC are described below. Many of these streams are normally vented to the atmosphere untreated since conventional VCM recovery systems cannot effect complete separation of VCM. The Tenneco activated carbon adsorption process can be effectively used to eliminate VCM emissions from the sources discussed below.

General PVC manufacturing process description - An excellent review of the chemistry and technology of PVC is given by Gottesman.[2]

Flow sheets for the manufacture of polyvinyl chloride resins via suspension and emulsion polymerization techniques are presented in Figures I and II. Generally, in these processes VCM and the polymerization initiator are dispersed in water by means of agitation or the use of suspending, or emulsifying agents; the polymerization temperature selected to obtain the desired molecular weight. The reaction cycle is terminated so as to optimize productivity, or earlier if enhanced porosity is required.

Due to polymerization kinetic limitations, conversion of 100% of the vinyl chloride to PVC is impossible. Usually, therefore, seventeen to twenty percent of unreacted monomer remains at the end of the polymerization cycle and this is recovered and recycled to the process. However, as much as four percent of VCM can be left in the reaction media because of the difficulty of removal. If this monomer is not removed from the suspension and emulsion slurries by specialized stripping techniques, it could eventually enter the environment. Therefore, EPA has proposed a limit on vinyl chloride content in resin leaving the stripping step. These limits are 2000 ppm for emulsion latexes prior to further processing to obtain product and 400 ppm for suspension slurries before they are sent to the filtering and drying operation.[7]

Slurry tank operation - Another source of VCM emissions is the slurry tanks where operators have historically purged air through the vapor space of the tank to keep VCM concentrations down and hence, minimize the chance of formation of a flammable mixture. Despite this precaution, some explosions have occurred and recent practice has been to blanket the tanks with nitrogen. Dependent on the level of stripping of the slurry downstream, VCM concentrations in the nitrogen purged (as the tanks are periodically filled) may reach 15 mole %.

Equipment purging with inerts - In various phases of the VCM and PVC manufacturing process, inert gas purging of equipment is required to reduce explosion hazard, remove last traces of VCM or to improve equipment efficiency. The off-gas purge streams generally contain 10-30 mole % vinyl chloride. Potential sources of these streams are (a) condenser purge,(b) VCM distribution systems, and (c) equipment preparation for maintenance and cleaning.

PILOT PLANT INVESTIGATION OF VINYL CHLORIDE ADSORPTION ON ACTIVATED CARBON

The following parameters were considered in the pilot plant investigation of VCM adsorption in the pilot plant:

Vinyl Chloride Monomer - The application of activated carbon for the adsorption of vinyl chloride has been explored in the laboratory by several workers.[3,4] These studies have utilized virgin (pure) vinyl chloride. Thus, they have not completely demonstrated the application of activated carbon adsorption to the VCM emitted from a PVC plant since the VCM studies by these investigators did not contain the number and concentrations of impurities which are usually present in the high VCM content gas emitted from the polymerization reaction. Adsorptive capacity and the long term utility of activated carbon in VCM service are strongly dependent

on the type of such extraneous impurities contained in the recovered monomer.

To our knowledge, Tenneco's pilot plant work is the first study conducted on the activated carbon adsorption with recovered vinyl chloride taken directly from a partially polymerized PVC batch. This recovered vinyl chloride monomer is considered representative of the typical composition of the emissions which can occur in a PVC plant. A comparison of the composition of virgin and recovered monomer is exhibited in Table I.

Recovered vinyl chloride may also contain residual initiators, catalyst fragments, and suspending agents, so that it is prone to auto-polymerize to form PVC. This in turn can foul a carbon system and greatly decrease its effectiveness over the long term. Therefore, it was necessary that operating conditions be selected so that polymerization on the carbon bed is avoided so as to obtain a practical service life at adequate bed capacity. Tenneco's carbon adsorption process, as finally developed, satisfies this performance criterion.

Carbon Evaluation - In order to demonstrate the effect of bed life and vinyl chloride adsorptive ability, three different types of carbon were investigated, each derived from a different source of raw material. They are described as Type A, Type B and Type C.

The data tabulated in Table III and graphically presented in Figures V, VI, and VII, give the results of tests conducted to determine the adsorption and desorption characteristics of several types of commercially available activated carbons. Type A carbon, Figure V, showed a gradual fall off in bed capacity from an initial 22.1% to 12.5% until the evaluation test with this carbon was purposely terminated after 82 cycles.

Type C carbon gave a lower initial bed capacity, 12%; however, the capacity held constant at this level for 82 cycles.

In Figure VI, data on the performance of Type B carbon are given. It is seen that this type of carbon showed a high initial VCM loading, but bed capacity fell significantly, to 6% after only 20 cycles.

The extensive data accumulated on these three carbons demonstrated that Type A carbon would consistently remove essentially 100% of vinyl chloride while providing long bed life.

Design basis - Based on analysis of actual plant process streams described in the previous section on sources of vinyl chloride emission,conditions were used which would potentially provide the most stringent conditions for the commercial carbon column.

Synthetic mixtures of unreacted vinyl chloride monomer with inerts were prepared by blending individual streams of each component. The flowmeters used in the study were very carefully calibrated with a wet test meter and a universal pump calibrator (Inspector Model 302). The results tabulated in Table II show remarkable agreement between theoretical and experimentally measured values.

Adsorption cycle - The schematic flow diagram of the pilot plant are shown in Figure III. Synthetic gas mixtures consisting of a desired composition of unreacted VCM and inert gases were passed in a downflow direction through the column containing activated carbon. A wide range of nominal velocities were investigated, ranging between 10 and 70 feet per minute. Exit gas samples were obtained at specified times and non-adsorbed VCM in the exit stream was monitored with a Hewlett-Packard 5700A Gas Chromatograph fitted with a Flame Ionization Detector with a sensitivity of 0.1 ppm. Gas samples were taken to the point at which the combustible gas detector showed VCM levels in excess of 0.1%. The vinyl chloride breakthrough profile shown in Figure IV shows that prior to breakthrough essentially 100% of the VCM is adsorbed by the activated carbon. An extremely sharp and substantial increase in vinyl chloride concentration occurs at breakthrough.

Regeneration cycle - The long term successful performance of activated carbon is highly dependent on the use of the proper regeneration procedure. From the pilot plant work, a regeneration procedure was developed which has been used in a commercial plant for well over 1300 cycles without noticeable deterioration of the adsorption capacity of the activated carbon.

Tenneco's regeneration process has been shown by sophisticated instrumental analysis to remove 99.4% of the VCM adsorbed in the carbon and to produce a regenerated carbon bed having essentially pre-regeneration adsorption efficiency. In Tenneco's regeneration process, even the 0.6% of VCM remaining with the carbon bed is not emitted to the environment.

Carbon analysis - After the cyclic tests, the carbon was removed from the unit and examined. There was no visible evidence of polymerization of VCM on the carbon or any change in color. The carbon samples were further analyzed by Soxhlet extraction with the extract also showing no indication of PVC. Surface area and pore size analyses showed no physical destruction of the carbon.

PERFORMANCE OF THE COMMERCIAL INSTALLATION

With the technical and economical feasibility of the adsorption route demonstrated on the pilot scale, the first commercial carbon adsorption unit for vinyl chloride was designed and built by

Chemical Design, Inc. of Lockport, New York. It was installed in Tenneco Chemicals' new PVC manufacturing facility at Pasadena, Texas in early 1975. A picture of the unit is shown in Figure VIII.

The adsorption equipment has been in operation for the past twelve months. During this time, the activated carbon in the test has undergone more than 1300 adsorption and regeneration cycles. The average VCM level, as monitored by a gas chromatograph analyzer on the adsorber effluent stream, has been less than 4 ppm.

After ten months of continuous service, samples of carbon were withdrawn from the adsorber and showed that the carbon had retained 90% of its original VCM adsorptive capacity. Further, there was no evidence of the polymerization of vinyl chloride in the adsorption unit or within the carbon.

Based on the above results, it is evident that for satisfactory performance and acceptable economics of a carbon adsorption unit, proper choice of the activated carbon and selection of optimum process conditions (adsorption and regeneration) must be made.

CONCLUSION

Based on the experience of a full year's operation of the commercial unit, it has been shown that activated carbon is a viable means of minimizing VCM emissions from a PVC polymerization facility. Selection of carbon and choice of operating conditions for the adsorption and desorption portions of the cycle are critically important to the success of such an installation. This, plus the variations of the composition of recovered VCM, make it prudent to carry out pilot plant work prior to design of such an activated carbon unit for VCM service.

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REFERENCES

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(2) Gottesman, R. T. (1975), Applied Polymer Science, A.C.S. Division of Organic Coating and Plastics pp. 349 - 384, Ed., Kenneth, J. and Tess, R.W.

(3) German Patent 2,148,954. 8/1/1974

(4) United States Patent 3,796,023. 3/12/1974 Raduly et.al.

(5) Wheeler, R.N., and Sutherland,M.E.(1975), Chemical Process Engineering, Vol. 71, No. 9, "Control of In-transist VCM".

(6) Immortino, N.R.(1975) Chemical Engineering pp 25-26, "PVC Makers Move to Mop Up VCM Emissions"

(7) U.S. Federal Register, December 24, 1975, Part II, EPA National Standards for Hazardous Air Products. Proposed Standards for Vinyl Chloride.

(8) U.S.Federal Register, October 4, 1974, Part II., Department of Labor OSHA Exposure to Vinyl Chloride, Occupational Safety and Health Standards.

(9) Cheremisinoff, P.N., and Morresi, A.C. (1974), Pollution Engineering, p.66.

TABLE I

ANALYSIS OF RECOVERED VCM vs VIRGIN VCM

Type Impurity	Virgin VCM PPM	Recovered VCM PPM
Propane	None Detectable	67
Propylene	0.2	30
Isobutylene	0.1	50
Propadiene	0.3	91
Butane	0.1	12
Butene-1	0.1	32
Methyl acetylene	0.1	9
Methyl chloride	47.0	845
Ethyl chloride	8.0	96
1,3 Butadiene	5.0	15
2-chloropropene-1	0.5	0.8
Acetylene	None Detectable	2
Ethylene	11.0	4

TABLE II

ACCURACY OF VCM GAS MIXTURE PREPARED USING FLOWMETERS

I. ANALYTICAL

THEORETICAL VALUE MOLE %	EXPERIMENTAL VALUE (GC) MOLE %
22	25
28	30
34	35
39	40

II. GRAVIMETRIC CHECK

SET	GRAVIMETRIC Cu.ft/hr	WET TEST Meter cu.ft/hr
10	0.033	0.0335
30	0.088	0.092

TABLE III

CYCLIC TESTS - VARIOUS ACTIVATED CARBONS - REPLICATION STUDY

RECOVERED MONOMER

Bed Capacity (lbs.VCM/lb. Carbon) x 100

Cycle Number	Type "A"	Type "B"	Type "C"
1	25.6	19.4	14.4
3	21.7	15.1	11.6
5	22.1	18.7	10.8
7	22.1	15.1	--
9	21.4	18.7	11.3
11	21.4	18.0	11.3
13	22.7	17.3	11.3
15	22.0	18.4	11.3
17	21.2	14.4	11.3
19	20.9	18.0	--
21	21.8	12.2	--
23	21.4	11.2	11.5
25	21.9	9.8	10.5
27	22.7	6.1	11.6
28	19.0	8.3	11.4
30	24.9		11.6
35	19.0		11.7
40	13.4		12.1
45	12.6		11.7
50	11.8		12.1
55	12.6		12.1
60	11.8		12.6
65	13.5		12.1
70	11.0		12.5
75	13.2		12.1
80	12.3		11.0
82	13.6		
85			
90			
95			

FIGURE I

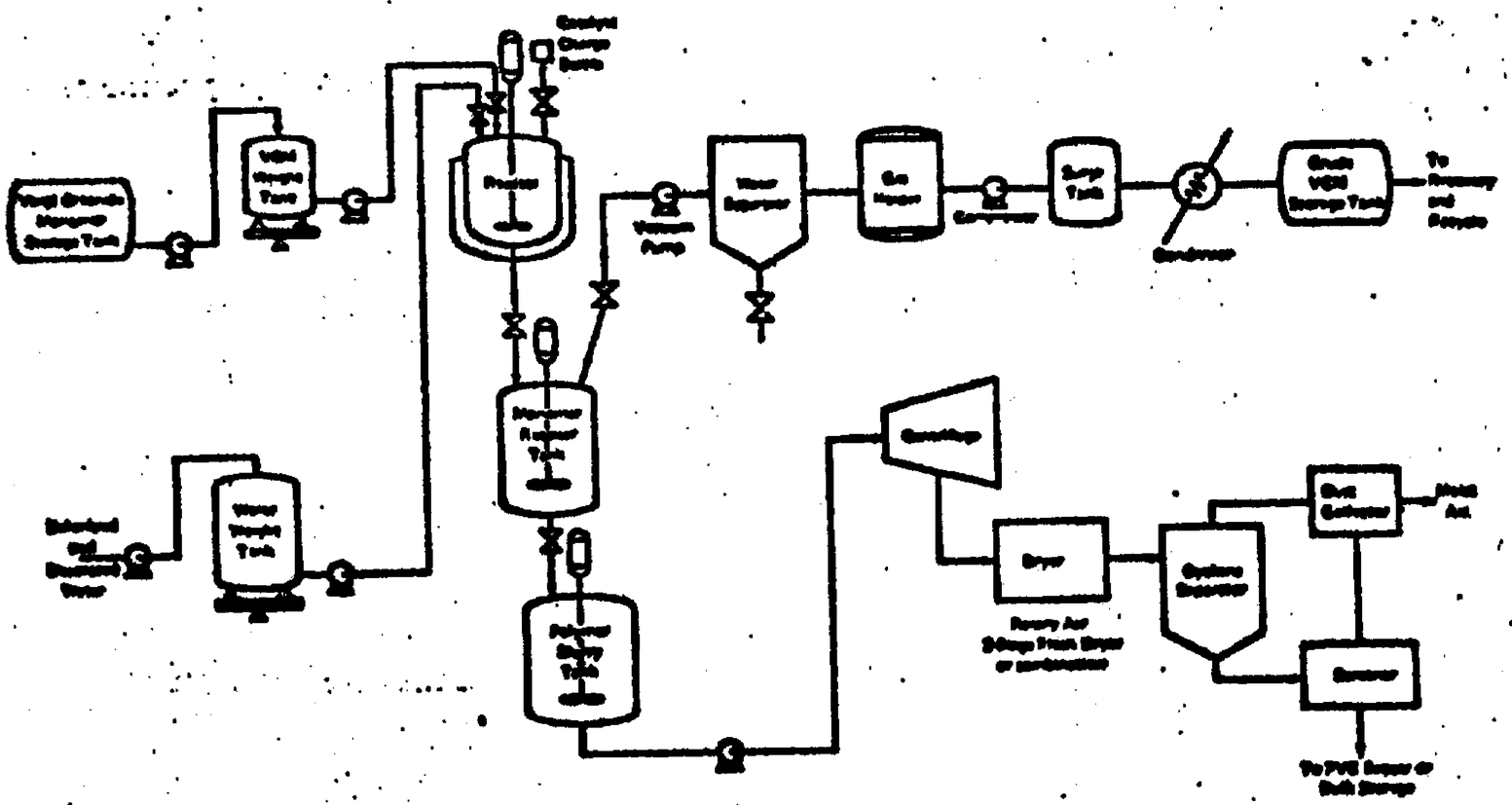

FIGURE II

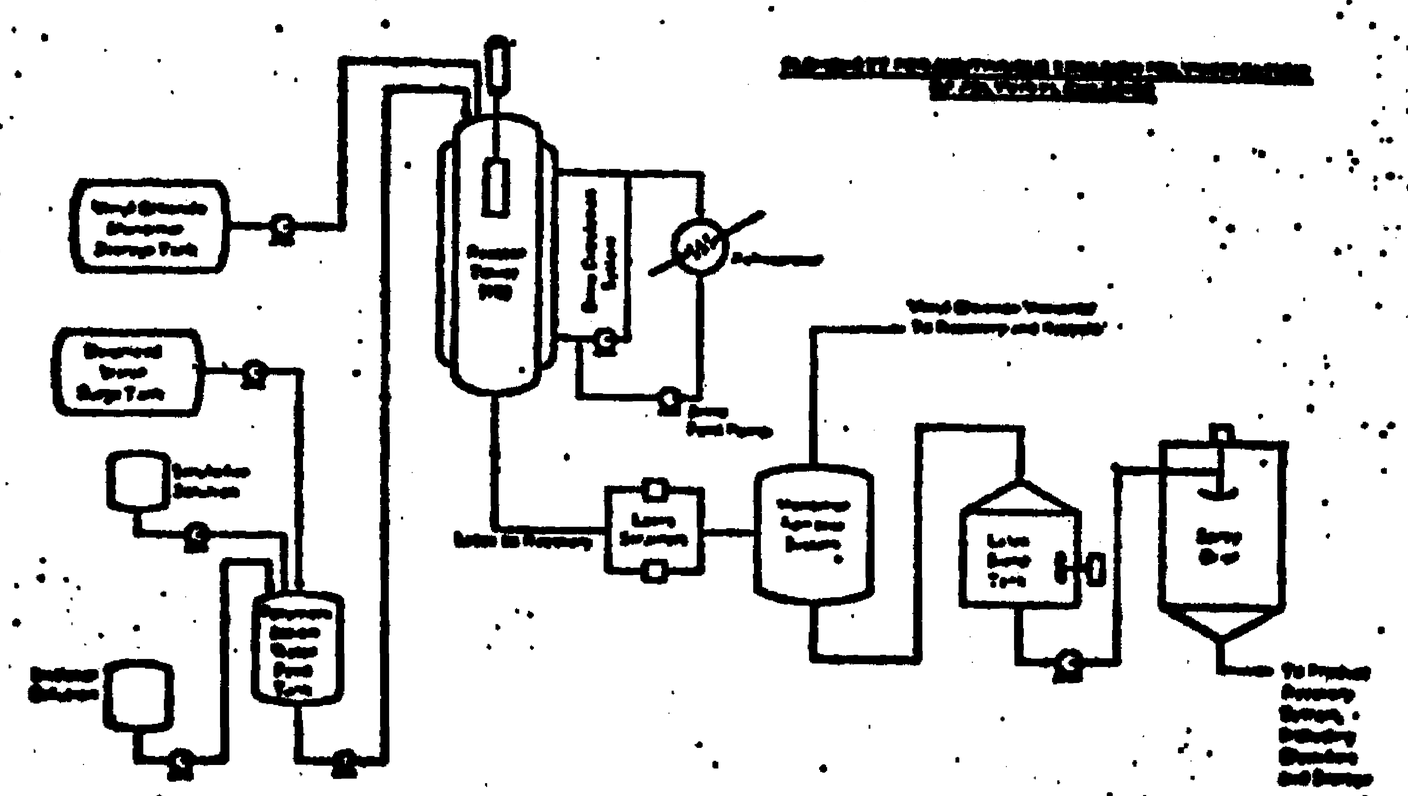

FIGURE III

SCHEMATIC DIAGRAM

PILOT PLANT CARBON UNIT

NAB 00011072D4

TO RECOVERY SYSTEM

CARBON COLUMN

REGENERATION SYSTEM

VCM SUPPLY

AIR SUPPLY

CONTINUOUS MONITORING PORT

SAMPLE PORT

FIGURE IV

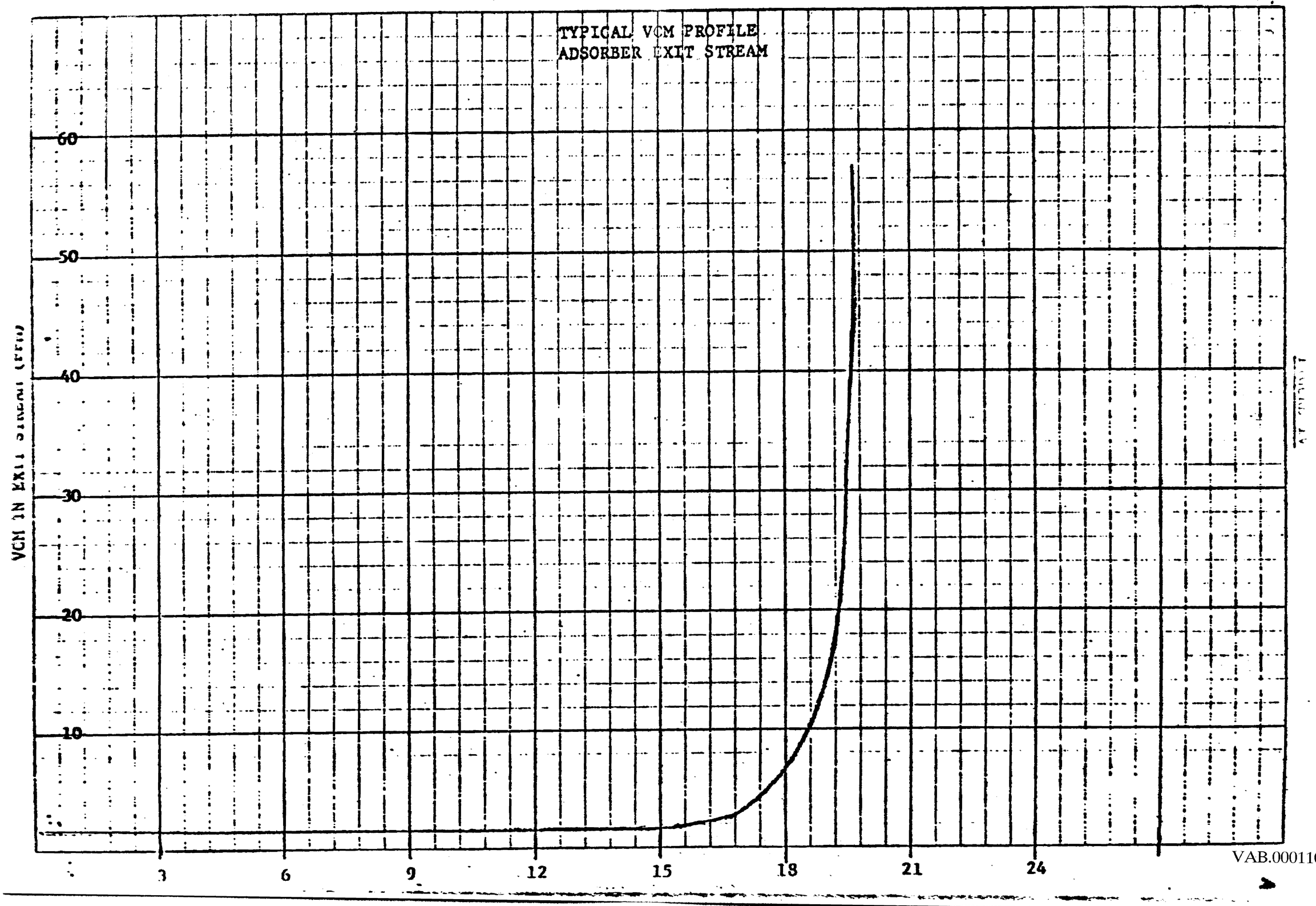

FIGURE V

EVALUATION OF ACTIVATED CARBON
TYPE "A"
CYCLIC TESTS

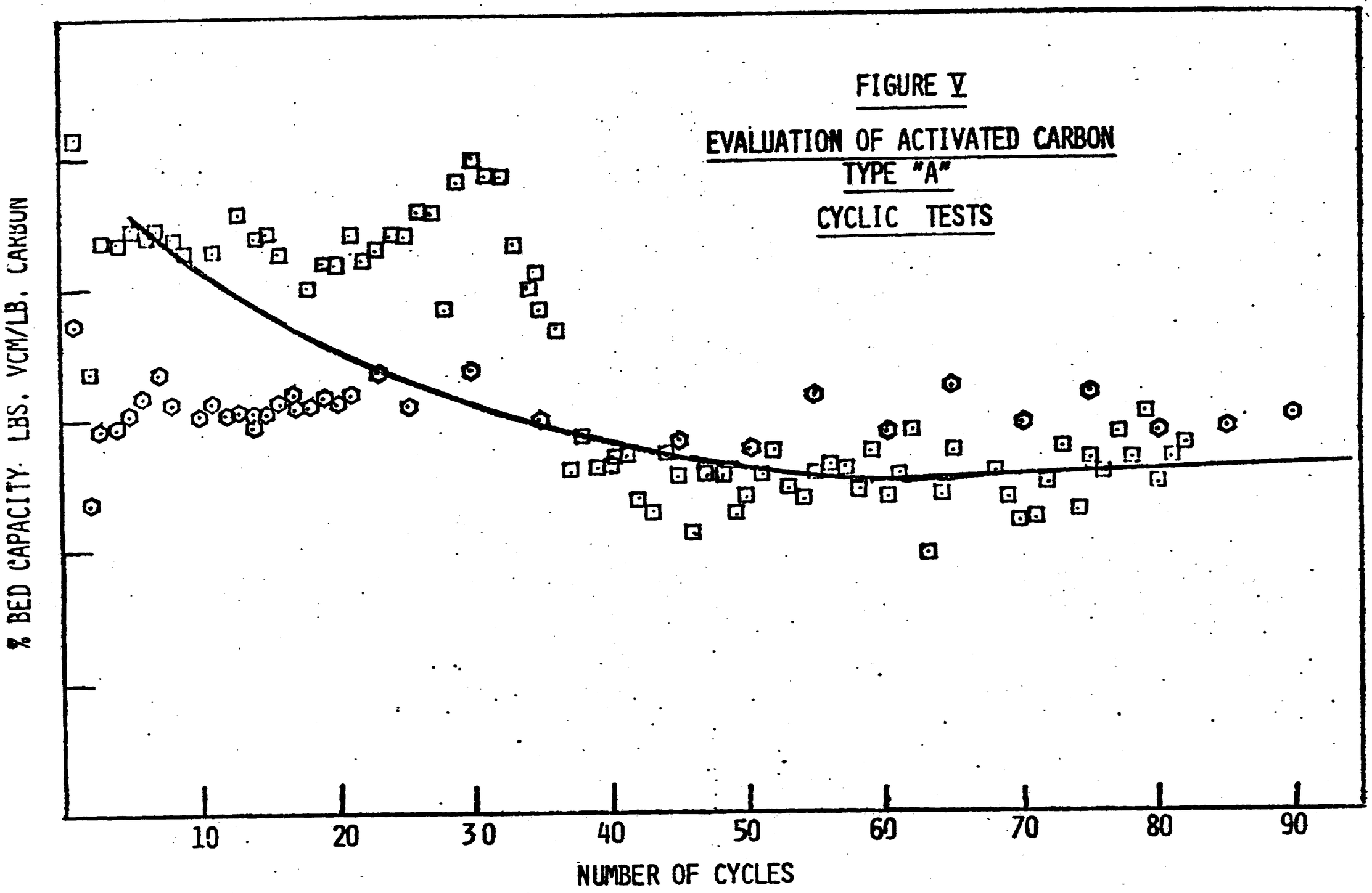

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FIGURE VI

EVALUATION OF ACTIVATED CARBON TYPE "B"

CYCLIC TESTS

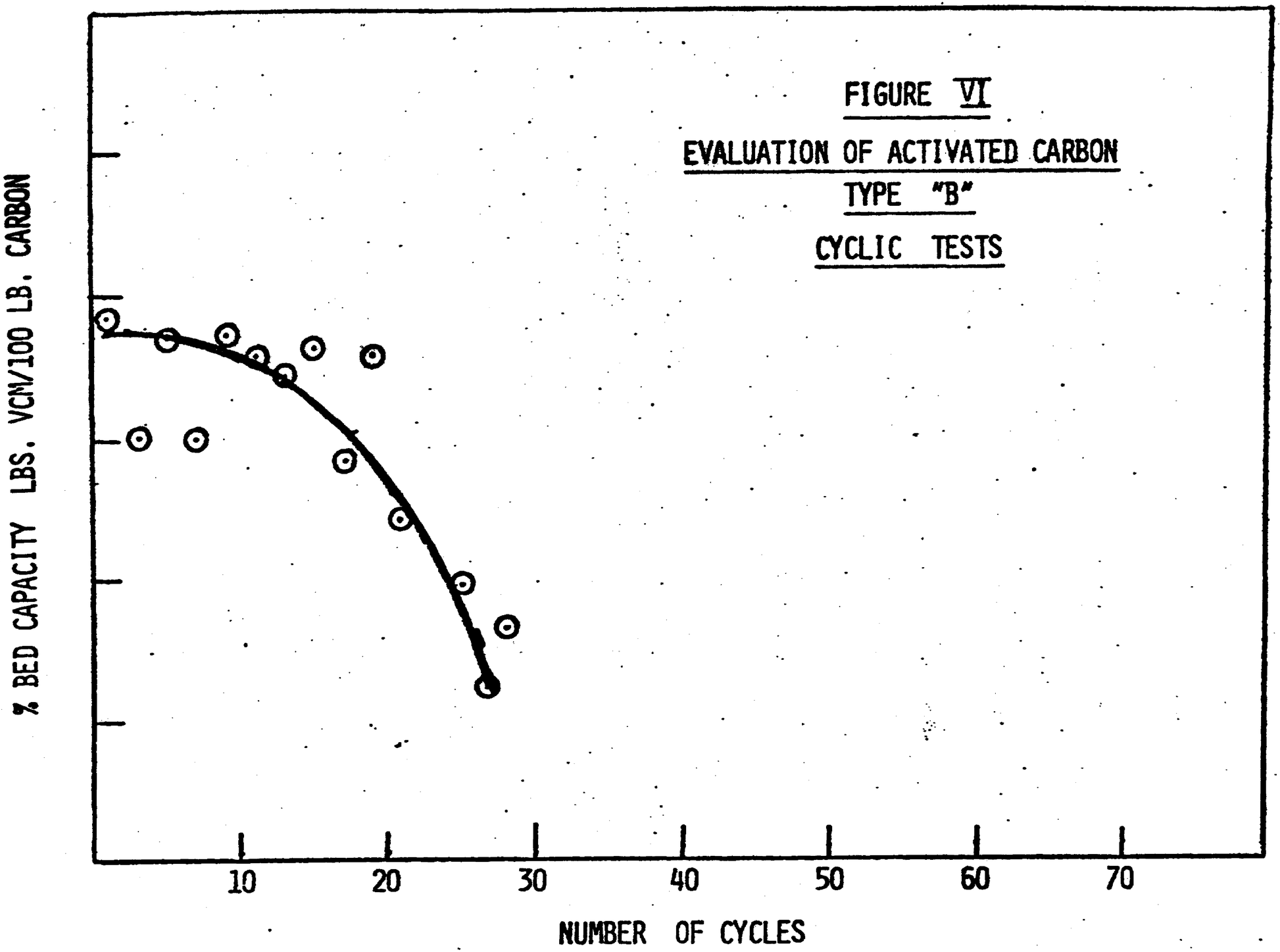

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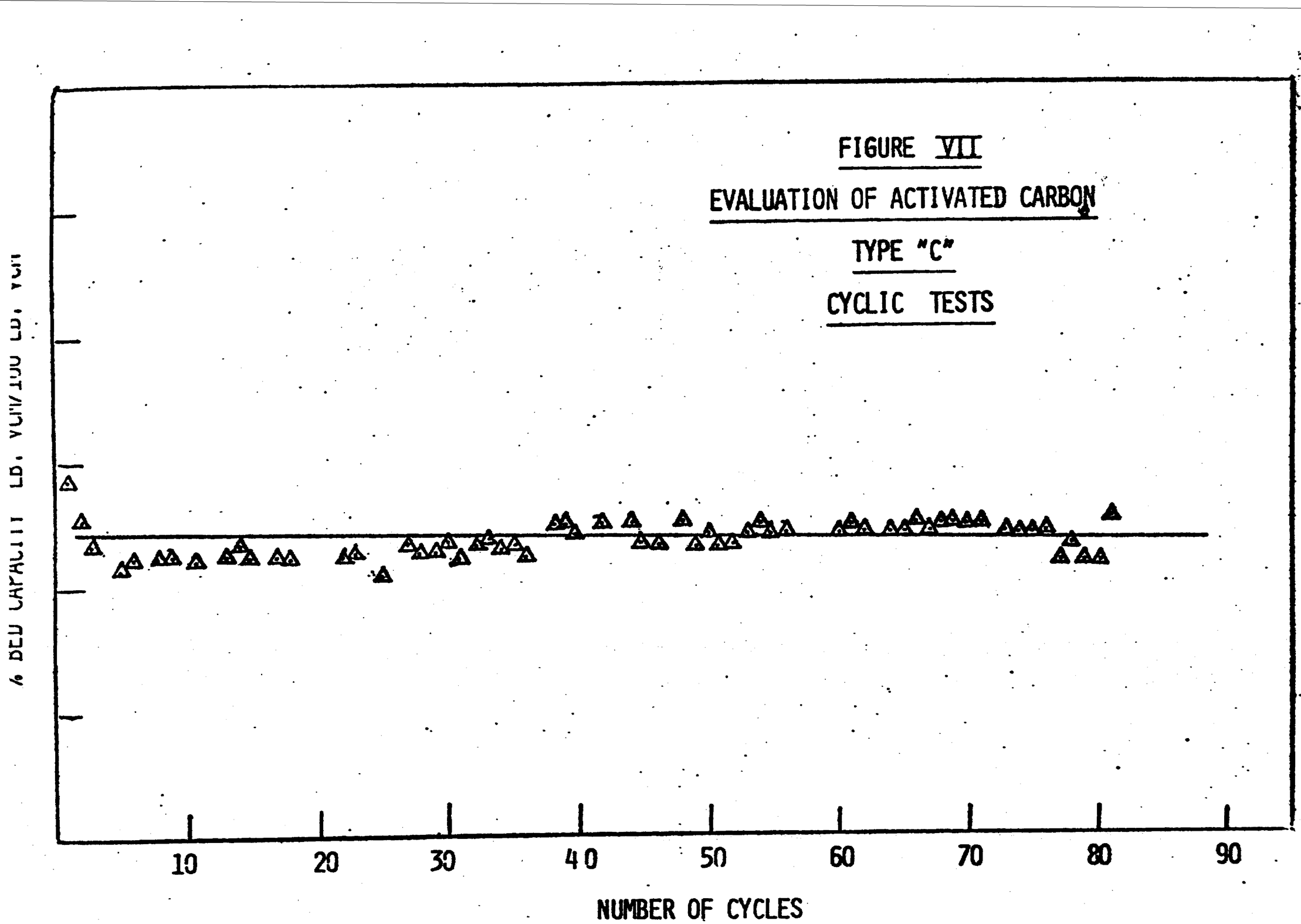
FIGURE VII

EVALUATION OF ACTIVATED CARBON

TYPE "C"

CYCLIC TESTS



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