EPA Settlement
(Air Products suit)

Chronology

Complaint filed	February 1981
Exchanged interrogatories	August
Draft settlement presented	August
Justice draft	November
Discussion	January 1982
Counterproposals	February, April
Handshake	June
Final	September (?)

Problems

Add equipment - dropped.
Stipulated penalties for NESHAPS - dropped.
Penalties for violation of decree - reduced, classified.
Possible Sec. 120 complaint - avoided.
Training - required for all, new and old.
- Competency test for new.
Causalty - lost.

Final Version of Consent Decree

Training, procedures (90/24, 9 months for Maintenance).
Logging of status, response
Penalties, cash and stipulated.
Time, 2 years operation or 3 years after restart.
New equipment to be covered also.

Air Products

Air Products and Chemicals, Inc.
Box 538, Allentown, PA 18105
(215) 481-4911

24 September 1982

Document Control Officer
TS-793, OPTS, Room E-401
401 M Street, S. W.
Washington, DC 20460

Gentlemen:

Re: Docket OPTS-50033

Air Products and Chemicals, Inc., submits herewith is comments on the proposal to amend 40CFR723.250 to provide a PMN exemption for certain polymers, as noticed at 47FR33924, 4 August 1982. We presume that these comments are required in triplicate, as were those of the companion Notice at 47FR33896, even though this Notice does not state that fact, and enclose three copies.

We oppose many of the requirements of this proposal, and believe that several other parts need clarification.

We agree with the concept of reducing the burden on the public and the Agency by providing exemptions to the current unofficial but established PMN procedures. We agree that many of the exemptions contained in this proposal are useful to that end, and should be approved. We do not agree with many of the proposed exclusions to these exemptions, for the reasons discussed below.

Air Products is a manufacturer of polyvinyl chloride (PVC) and polyvinyl alcohol (PVOH) both of which would be denied exemptions under this proposal, despite the fact that both have been used safely for many years in food, drug, cosmetic, and medical applications. Therefore we conclude that the criteria for exclusions from the exemptions have been formulated improperly, and we present our reasons below for that conclusion.

We have commented on the companion proposal for site-limited and low-volume exemptions, Docket OPTS-50032A, 47FR33896. Many of the general comments there are applicable here also, and we ask that those comments be incorporated by reference in this docket.

We are members of the Chemical Manufacturing Association, and have reviewed a draft of their comments on this matter. We support their comments generally. In particular, however, we believe that their proposal for an expedited PMN rather than exclusion from the exemption is a worthwhile suggestion and we urge your careful consideration. If the Agency is unwilling to remove such demonstrably safe classes of polymers such as the PVC's and PVOH's from the exclusion list, it should at least allow them an accelerated PMN. However, we see no reason why those classes should be singled out for any special treatment.

We appreciate the opportunity to comment on this proposal, and will be happy to discuss any of these points further if that is discussed.

Sincerely,

AIR PRODUCTS AND CHEMICALS, INC.

John T. Barr
Regulatory Response

JTB/cay
Attachment

bcc: A. J. Diglio
J. Dubeck - Keller and Heckman
F. Licktenberg - SPI

Comments On

Proposed PMN Exemption for

Certain Polymers

Docket OPTS-50033

47FR33924

4 August 1982

by

Air Products and Chemicals, Inc.

30 September 1982

AP00018781

Table of Contents

Table of Contents

(continued)

AP00018783

I. Introduction

We understand, of course, that this rulemaking will not affect current inventoried products directly. It will have, however, significant indirect effects.

There will be a stigma attached to any product class which is excluded by this proposal, because of the suspicion that the exclusion rule implies a potential for some hazard.

There also will be an important effect on new product development, especially on the flexibility of producers to make adjustments in the composition of a product to meet changing needs of a customer or to adapt to new uses.

This burden will fall particularly hard on small manufacturers, or on small volume specialty producers where the resources may not be available to meet the complex technical demands for exemption which are proposed here.

It appears that this proposal is not intended to cover the large class of high molecular weight polymers which are termed "structural". There is no reference in the Notice to the several communications which the Society of the Plastics Industry, Inc. (SPI) has had with the Agency, and structural polymers are not discussed. The thrust of all the discussions seems to be toward low molecular weight materials. Further, the worker exposure assessment document by Mitre Corp. (ref. 50 of the Notice) states on p. 3 that the substances studied "are not the structural polymers as described by the Society of the Plastic Industries, Inc.", and references the SPI position paper of August, 1981 describing its proposal to exclude structural polymers from the inventory, as do the European rules.

Had the Notice been clear about the relationship of structural polymers to this rulemaking, it may have avoided much of the concerns that the Notice has caused. We cannot proceed on assumptions, however, and our comments speak to the Notice as it appeared, without any statement distinguishing structural polymers.

In addition, much of the effort seems misdirected toward monomers which already are on the inventory, and thus are not subject to PMN rules.

We will discuss first the proposal as it applies to the two classes of polymers of particular interest to us, and then present general comments on other aspects of the proposal.

II. Polyvinyl Chloride (PVC)

Except for its coverage by the proposed exclusion of 40CFR723.250(d)(5), PVC (homopolymers and copolymers) meets all of the criteria for the exemptions of this proposal. The Preamble states at p. 33928, in sec. 3B5 that the only reason for this exclusion is concern for residual monomers. Vinyl chloride (VC) is named specifically there, although misspelled. On the face of it the exclusion is incorrect, because not

all chlorine - containing polymers are made from vinyl chloride. Other major families of chloride - containing polymers may be made from chloroprene, vinylidene chloride, chlorofluoroolefins, and so on. Vinylidene chloride was reported by the National Toxicology Program (Fiscal year 1982 Annual Plan, page 87) not to be carcinogenic in rats or mice in report NTP-80-082, TR228, NIH publication 82-1784. Chloroprene is stated in that same report not to be mutagenic in the Ames test (p. 52, item 34 of Table 2). Thus it is improper to state a concern for the toxicity of all chlorinated polymers because some may be prepared from vinyl chloride, which is toxic, when there is not evidence of similar toxicity in other monomers also covered. A regulatory decision based on such a position would be an arbitrary misuse of regulatory discretion.

However, directing attention to only PVC and its principal monomer, the Agency does not seem to be aware of the current regulatory status and safe use of these materials.

A. Current Regulatory Status

1. Food and Drug Administration

PVC currently is approved and/or has prior sanction for use as food contact components, components in packaging materials, and in paper (21CFR175, 178). The FDA proposed to withdraw the prior sanction for food contact for rigid forms in 1975 because of concerns for residual monomer, but announced this year that it will withdraw that proposal. See the "Second Annual Report on Carcinogens", National Toxicology Program, Public Health Service, December, 1981 (Issued May, 1982), page 240. The 1975 notice stated specifically that the status of plasticized PVC was not to be changed. In plasticized form the product is used in blood bags, transfusion and drainage tubing, food conveyors, and many other critical applications. Thus, PVC is not inherently harmful, if processed properly.

This point is supported by the Mitre Report (ref. 50) referred to above, which states each time applications of PVC are discussed that consumer and environmental exposures are negligible. See, for example, pages 88, 97 and 107 of that document. The vinyl chloride emulsion copolymers (EVCl) are approved for use by FDA under 21CFR175.300 and 176.170.

2. Occupational Safety and Health Administration

The Notice states that one of its concerns is exposure to residual monomer during processing. OSHA established (29FR1910.1017) a standard for occupational exposure to VC which sets an action level of 0.5 ppm (8-hr. TWA) below which the standard does not apply. This action level effectively exempted processing and fabrication plants from the OSHA standard because the residual level of monomer in PVC is so low that the action level is not exceeded.

AP00018785

Thus, polymers of vinyl chloride can be processed safely, in accordance with the very rigid exposure standards which are imposed on them.

This position also is supported by the Mitre report, which states on p. 4:

> There is normally little potential for workplace exposure to high molecular weight thermoplastic resins used for injection molding and extrusion.

3. Environmental Protection Agency

This Agency has a standard (40CFR61.60) for environmental release of VC. This includes among other provisions, that suspension polymers, which use over 85% of the VC consumed in this country, must be stripped to less than 400 ppm residual monomer on a dry basis before contact with the atmosphere (there is an alternative of controlling dryer off-gases, but all U.S. producers have chosen the stripping method for compliance.) Voluntary industry agreement have reduced this to 10 ppm in the finished polymer for the majority of products which go into consumer goods, which provides further protection for fabrication employees, consumers, and the environment. See EPA 450/3-82-003 for further details on this point.

This Agency recently approved a test marketing exemption for a vinyl chloride-ethylene copolymer. See 47FR38632, 1 September 1982, TM-82-44. This Notice states that the Agency has established that this approval will not present an unreasonable risk of injury to health or to the environment because of low health and ecological concern for this polymer.

The EPA and FDA have a memorandum of understanding signed 12 June 1979 by the Administrator which assigned to the Agency the responsibility of controlling direct and indirect additives to drinking water, which would include any leechate from pipe.

Waste disposal is regulated by the RCRA rules, and other spills and releases are covered by the CERCLA regulations. Under these, VC and PVC are literally covered from the cradle to the grave by several stringent and all-encomposing standards.

Thus, the environment, the worker, and the consumer are protected from adventitious VC by existing regulations. Adding to this safety is the fact that VC migrates slowly, if at all, from finished forms under use conditions. Emissions, if they occur, do so only under heat processing. OSHA regulations cover this step.

Therefore, we seen no reason for EPA to be concerned about potential exposure to the environment or persons from existing PVC use. Any new VC-containing products are covered by

AP00018786

the existing OSHA-EPA rules, and cannot be produced outside of their control. Thus, there is no reason for concern over possible future exposure from new products.

In addition to providing considerable assurance that no harm comes from the manufacturer use of PVC, the facts recited above lead to the conclusion that the Agency may not regulate vinyl chloride polymers under TSCA. Section 9 of the TSC Act requires that efforts be made to regulate potential hazards under existing statutes and regulations before TSCA is invoked. Regulation of PVC because of concern of exposure to its residual monomer under this proposal would be a duplication of regulation, which is forbidden by Sec. 9.

Further, because VC is on the inventory, its presence in polymers would be defined as a mixture, which is not subject to TSCA rules. See the discussion on p. VI-12 of support document 54 of this Notice, for a further discussion of this point. There it is stated that monomers are not subject to 5(h)(4) regulation.

This proposal, therefore, appears to be an effort to bypass Sec. 5 of the TSC Act, and to produce an unauthorized SNUR requirement for inventoried monomers. These are strict procedures delineated for SNUR actions, and this proposal does not conform to those requirements.

If the Agency has concern for the hazards of certain monomers, it has available the Sec. 4 Test Rule procedure, and should not attempt to regulate such materials on suppositions outside the statutory mandate.

Therefore, the Agency may not regulate PVC, or other polymers, for the reasons stated in Sec. III B 5 of the preamble unless or until it has determined that the existing regulations or the other remedies available to it under the statutes cannot and will not control the potential hazard. We do not believe that such a determination can be supported by fact.

B. Eligibility for Exemption

The proposal specifies several criteria for exemption. Each of these is discussed below with reference to PVC.

1. Molecular weight

Exemption is offered to polymers with number average molecular weights of greater than 20,000. The commercial polymers and copolymers classed as conventional PVC have weights of 65,000 - 120,000. Those below this range are too brittle for satisfactory service. Those above this range have very difficult processibility, and are not useful.

Other less well-known copolymers of VC, termed "EVCl", are made utilizing ethylene, for example, as a comonomer. These are prepared in emulsion form, and have molecular weights in the range of 50,000-90,000.

AP00018787

2. Polydispersity

Conventional PVC has a polydispersity of about 2, and the emulsion copolymers have a value of about the same range. This is well within the allowable values of Table 2 of the proposal. There is essentially no polymer with a weight below 1,000 present in the commercial products.

Therefore polymers and copolymers of VC which have commercial utility meet all of the requirements of the proposal paragraphs (e) and (f), and are excluded only because of chlorine content.

We have shown above that the potential for vinyl chloride exposure is regulated strictly by existing regulations, and that current products are approved for a wide range of consumer and medical applications, and are being used safely and satisfactorily in those applications.

We see no reason why new products containing VC would not be equally safe, as they would be covered by the same regulations. The OSHA and EPA regulations apply to any place where vinyl chloride is present or is used in polymers to any extent whatsoever. We therefore request that the Agency remove the exclusion from the proposed exemptions as it applies to polymers and copolymers of vinyl chloride.

We fully expect most types of PVC will be exempt from all inventory requirements under any forthcoming structural polymer rulemaking. Nevertheless, we also believe that it is proper for the Agency to include new variants of PVC under the exemption of this rulemaking, so as to avoid unnecessary inhibition of innovation and impact on foreign trade which the present PMN procedures impose (see 47FR33910, 33913, and 33917-18).

III. Polyvinyl Alcohol (PVOH)

Polyvinyl alcohol is the product of hydrolysis of polyvinyl acetate (PVAC), a homopolymer of vinyl acetate (VAC). All or most of the pendant acetate groups are removed by hydrolysis or saponification of PVAC to give a material containing only carbon, hydrogen, and oxygen, with the structure - $[CH_2CH(OH)]_n$. It is a stable, nontoxic polymer and is water soluble to various degrees, depending on the completeness of removal of the acetate moieties.

Therein lies the problem. This causes PVOH to fall under the proposed exclusion of (d)(1) - water soluble polymer. Also, unfortunately for this proposal but fortunately for the environment, it is biodegradable, and thus falls under (d)(7) also.

PVOH was not necessarily designed to have these properties, it just turned out that way. Extensive use of PVOH has resulted from its water solubility, but it also has applications in films, coatings, fibers, and molded products. We do not understand the Agency reasoning as to why these properties are deemed to be harmful, and as is discussed below, we believe that PVOH should be removed from the exclusion because of its lack of potential for harm to the environment.

AP00018788

A. Current Regulatory Status

PVOH has approval and/or prior sanction for use as a food contact surface component, an adhesive component for packaging materials, and a color additive diluent under 21CFR175-178 and 181. It is listed in the U.S. Pharmacopiea as a viscosity - increasing agent and as a pharmaceutic necessity for opthalmic solutions. Both it and its precursor PVAC have a long history of safe use in many food and consumer applications.

There is no residual monomer in the final product. The production process includes an extractive distillation which recycles the unreacted vinyl acetate. Even if it were present, VAC has a low toxicity. Its hydrolysis products are natural components of the human metabolic process. See DHEW-NIOSH Pub. No. 78-205, 1978 "Criteria for a recommended standard - workplace exposure to vinyl acetate" for a summary of the toxicity of vinyl acetate.

The precursor polymer, PVAC, is also nontoxic, and is used as a base for chewing gum and many other FDA-approved applications. Thus, even if there were any residual monomer or precursor polymer, there would be no toxic hazards from their presence.

The lack of toxicity of PVOH which permits these applications is well established. Earlier data have been reviewed in "Kirk-Othmer Encyclopedia of Chemical Technology", volume 21, 2nd edition, p. 359 (Interscience, 1970), and the "Encyclopedia of Polymer Science and Technology", volume 14 (Interscience, 1971).

In summary, these reviews referred to above show that oral administration of PVOH to rodents causes no chronic effects, and there are acute effects only at doses over 2g/Kg/day. See: Platzer, Mod. Plastics 28 (7) 95 (1951); Inskip and Peterson, Mod. Packaging 30 (1) 137 (1957); Lefaux, Chemie und Toxikologie der Kunstoffe, Verlag, Mainz, 1966, pps. 292-295; Babev, Azerb. Med. Zh., 56 (10) 18 (1979). PVOH is not metabolized by humans. Very low molecular weight substances, if present, pass through the liver and kidney to the urine; the higher polymers remain in the feces ("Elvanol", duPont, Wilmington).

Efforts were made to use PVOH as a blood extender, but it was found that at the higher concentrations where it would be most useful, it caused coagulation of the blood, so this use is not commercial. See: Kainer, "Polyvinylalkohol", Enke, Stuttgart, 1949; Danishevski, et al., "Toksikol Vysokomol Mater Khim", Inst. Polim. Plast. Mass, pps. 94-105 (1966); Grigoryan, et al., Z. Kh. Partev. (Tiflis) (1967) 10-11, 113-116; Hueper, et al., J. Pharmacol. Exptl. Therap., 70 201 (1940). Otherwise, injection of solutions caused no toxic effect. See: Hueper and Kainer, op. cit. and Zaeva, et al., Tokoikol. Novykh. Prom., 5 136 (1963); Weil, J. Pharm. Belg. 18 (45) 445 (1963).

AP00018789

Unpublished results obtained by Air Products at Biosearch, Inc. of Philadelphia, Pa. in 1978 and 1979 show that neither the powder nor aqueous solutions of PVOH are primary irritants to rabbit eyes or skin, whole or abraded. Rats were exposed to as much as 24 mg/m^3 of 3-5 micron PVOH dust without effect, and gross pathological examination 14 days later "revealed nothing remarkable".

Thermal decomposition of PVOH at 200°C and up yields primarily water and char with small quantities (about 1%) of alcohols, ketones, and aldehydes (Finch, "Polyvinyl Alcohol", Wiley and Sons, New York, 1973).

RETECS classifies PVOH as an animal carcinogen, and cites Vol. 19 of the IARC series as the reference. That volume discusses only various subcutaneous implantation tests. These were found to produce local tumors if the correct size particles were used. Powders did not give this effect, platelets of mm size range did. This is a well-known effect which almost any solid substance will produce [Ziche and Gullino, Can. Res., 41 5060 (1981)]. It is the result of the universal foreign body reaction, and is not accepted as a carcinogenic response. See, e.g., Brand "Foreign Body Induced Sarcomas" in Becker (ed.) "Cancer, a Comprehensive Treatise", Vol. 1, pps. 485-511, Plenum Pub., New York, 1975. OSHA excludes implantation site tumors of this type from classification as an indicator of a carcinogen. See: 29CFR1990.144 (b)(11), 45FR5287. The cited IARC volume states (p. 359) that they draw no conclusion as to carcinogenicity from these data.

Thus, the classification by RETECS is improper, and is not accepted by the scientific community. It makes the same error for PVC, polyethylene, and many other materials accepted as innocuous. Further, PVOH and these other materials are used successfully as surgical implants (Kirk-Othner and IARC, loc. cits.) in both humans and animals. We therefore conclude that PVOH is not a "carcinogen" within the general meaning of the term, or as it is used here by the Agency.

B. Eligibility for Exemption

1. Polydispersivity

The attached table shows the molecular weights and calculated PD values for our commercial grades of PVOH. The M_n values can be seen to range from about 28,000 to about 110,000. The PD values are generally in the 115-210 range. This value indicates a somewhat narrow molecular weight distribution, and allows essentially no material below 1,000 to be present.

Therefore, PVOH is acceptable for exemption under this proposal so far as PD values are concerned.

AP00018790

Table I

PVOH Molecular Weights

by GPC/LALLS

Sample	#	DPN	DPW	$\bar{M}_N$	$\bar{M}_W$	$\bar{M}_W^*$	$\bar{M}_W/\bar{M}_N$
V205	04080706	24,800	49,600	28,200	41,100	42,800	1.46
V523	09110327	59,800	119,600	67,800	130,300	138,000	1.92
V540	701090230	109,400	218,800	110,300	181,900	174,900	1.65
V107	04080706	22,300	44,600	27,800	43,200	35,100	1.55
V325	07090887	53,700	107,400	57,800	105,800	107,000	1.83
V350	04100680	98,100	196,200	79,800	152,900	131,400	1.92
WS42	02110190	-	-	42,800	90,400	99,500	2.11

DPN = Number-average MW from degree of polymerization
DPW = Weight-average MW from degree of polymerization
$\bar{M}_N$ = Number-average MW from GPC/LALLS
$\bar{M}_W$ = Weight-average MW from GPC/LALLS
$\bar{M}_W^*$ = Weight-average MW from static LALLS (KMX-6)

2. Biodegradability

For many years PVOH was thought to be nonbiodegradable, and achieved some utilization as a replacement for starch as a textile sizer because of this (Finch, loc. cit.). In fact, it is fairly easily degraded after some acclimatization of the flora, and degrades completely to carbon dioxide and water. The attached reports from our laboratory give the details of both laboratory and large-scale tests which illustrate this property. Attachment I, Casey and Manley "PVOH Degradation by Oxygen-Activated Sludge", Third International Degradation Symposium, August 1975. Attachment II, April 1, 1982 letter from J. P. Casey to a customer.

We believe biodegradability to be an asset, and not a liability as this proposal claims. This is especially true when the degradation goes to completion, as is shown in the attached data. No harm can come to the environment from either the material itself or its degradation products. The degradation process is seen to be nontoxic to ordinary populations of bacteria in sewage effluent, and thus does not interfere with other biological processes, or pose a threat to the environment.

Our conclusion is that PVOH is an innocent product which happens to have fallen into the net spread by the Agency in its concerns for possible new hazards. We believe that it should not be excluded from the potential exemptions. It should be noted that if starch were to be discovered after this rule became effective, it would be excluded for exactly the same reasons as PVOH - water solubility and biodegradability. (Sugars, of course, fall into a third excluded group - low molecular weight.)

One way out of this untenable situation would be to grant blanket exemption to all polymers containing only the atoms carbon, hydrogen, and oxygen. Failing that, known nontoxic functional groups, such as the aliphatic-OH group, could be made another prerequisite, as it is in (d)(6)(ii) for functional groups as a class. We urge the Agency to consider seriously this approach so that it is not put in the anomalous position of excluding recognized pharmaceuticals such as PVOH or major foodstuff such as starch from the exemption.

IV. Economic Impact

We believe that the economic analysis present in the preamble at Sec. IV B is defective on several points. These are discussed below.

A. Cost of Compliance

The economic impact of this proposal is based largely on an unrealisticly low estimate for performing the tests necessary to provide the information needed for the exemption notice. For example, a cost of about $400 is used for a chromatographic analysis to measure molecular weight distribution. That figure can be correct only for repetitive analyses of a well-characterized material in a laboratory equipped to perform such analyses routinely. However,

AP00018792

this proposal applies to new substances. Because they are new substances, it will be necessary first to calibrate the apparatus for this new polymer. This is a research project of some magnitude, and requires extensive time, technical resources, and of course, money.

For example, until very recently the standard method to determine the molecular weight of PVOH was to reacetylate it to PVAC so that it was soluble in the conventional organic solvents, and to determine the molecular weight by GPC. This was a satisfactory procedure, but gave only an indirect value for partly hydrolyzed products and required correction for the estimated degree of hydrolysis.

After a three-year search for a more suitable method, we have now concentrated our efforts on a new direct procedure using low angle laser light scattering. Development of this procedure, after we had settled on an analytical method, required about 4 more months of labor over the period of nearly a year. Direct charges for just the last phase of this project were $22,000, plus a small amount of effort allocated to another project. This does not include equipment costs, or general administrative overheads.

After full development of this method our repetitive costs will be low. However, when we produce a minor variation of our standard polymers, at least a portion of the validation and calibration work must be repeated to assure ourselves that the procedure is appropriate. A major variant or a new polymer will require about as much effort as did the above exercise. Thus, we cannot agree that $400 is a reasonable figure for a PD determination on a new product. It is for this reason of cost that such determinations are not used routinely as quality control measurements, but are reserved for research projects.

This burden will fall most heavily on a small manufacturer who must either provide such equipment, costing $50,000 and up, and then establish the necessary skills and calibration, or depend on outside laboratories, where the costs and delays are likely to be large.

Similar comments apply to the required fractionation effort to determine the low-molecular weight content. This is still largely an art, not a well-developed science, and no generic procedures can be established for this step. Each study becomes a separate research project, consuming much time, and requiring considerable expenditures.

Because of errors such as these in the cost analysis, the economic analysis is incorrect.

B. Benefits of Compliance

We see little incentive for a producer of a new polymer to use the exemption procedure. The largest incentive seems to be a postulated saving of 90 days or so in the ability to proceed with production.

AP00018793

This is a phantom incentive. At the time the manufacturer has the commercial and scientific data at hand to proceed with scale-up, there is the option to submit either a PMN or an exemption request. The PMN can be prepared and submitted in a few days. The exemption data development can take days or weeks to obtain, and results in data useful only to one specific variant of the product. Thus the time saved will be less than 90 days by some unknown factor, the cost will be greater, and the resulting permit will be far less flexible as to further production variations than would a PMN approval.

Actually, the incentive is not to avoid a 90-day PMN examination, for there are other alternatives available to a producer. These include the TME, for which there is a 45-day period, the low volume and site-limited exemptions of proposed 40CFR723.10 (Docket 50032A) which requires simply a notice for materials of this molecular weight, or the Research and Development route, all of which allow production of specified amounts with lesser waiting periods than for a PMN. A potential producer will evaluate each of these alternates before choosing the more laborious route of this proposal.

In addition, the excessive record keeping that is required under an exemption as compared to that for a normal PMN procedure is further disincentive for choosing this route.

C. Saving of Agency Resources

The discussion above leads us to believe that only a small portion, if any at all, of new polymers will be processed through the exemption route, and any predicted reduction in Agency work load will thereby be diminished.

In addition, we understand that the Agency now completes most, if not all, of the polymer-related PMN's in about 14 days. This is confirmed by a comparison of the submission and approval dates for polymer PMN's and TME's appearing in recent issues of the Federal Register. Therefore, there will be no significant reduction in burden achieved by the mini-PMN process proposed here. There could be an increase if more data must be evaluated.

Perhaps most significant of all, these exemptions are valid only for some vague and undefined "conditions of the exemption", and the full PMN process must be employed if these "conditions" are exceeded. See the discussion of preamble Sec. III B. Therefore we fail completely to understand how a claim for benefit can be developed from failure to place these new products on the inventory. It will be necessary to go through the PMN process anyway if the product is a commercial success. (Of course, the SPI proposal to remove structural polymer altogether from the inventory would result in a large savings of resources by both the Agency and industry.)

AP00018794

Further, our expectation is that in many cases the producer will elect to utilize both routes simultaneously as assurance of a positive response. This will only serve to increase the burden of the Agency.

Therefore, for these reasons, the economic impact is invalid. We believe that this proposal, in those instances where it may be used, will not provide a significant burden reduction to industry or the Agency.

V. Technical Comments

There are several technical errors in the proposal which are worthy of comment.

A. Polydispersity (PD)

This value is, as stated, one method of measuring the range of molecular weight of a polymeric mixture. Because of this, PD values of 1.0, or any value near that figure, are impossible in mixtures of polymer species. That value is possessed by only discrete chemical substances, not polymeric mixtures. See p. V-19 of support document 54 of this proposal for further discussion of this point. Table 2 of the Notice is the result of the expansion of an arbitrary mathematical expression designed apparently to give assurance that amount of low molecular weight material though to be undesirable are not present. It bears no relationship to real-life situations, and should be abandoned for a more realistic parameter. If fractionation is to be required, then there is no need for this criterion.

B. Exemption Wording

The content of proposed sec. 723.250 (e) (3), the PD exemption criteria, suggests that it applies only to polymers in the range of 3,000 to 20,000. If this is correct, it should be stated clearly. However, as discussed above, we doubt the scientific validity of the basis for this exemption.

Note that there appears to be a typographical error in the values of PD in Table 2 for the molecular weight range of 4,000 to 4,999. We also are very doubtful of the ability of molecular weight determination to produce results accurate to four significant figures, as is implied by Table 2 of the Notice. Our experience is that M_N can be determined to about ±5-13%, and M_w to ±3-7%. Thus there can be as much as ±20% variability in PD as calculated from these data. This experience is supported by statements in cited reference 51 of this proposal at pages 53 and 71, and in docuemnt 54 at p. V-6.

C. Scope of the Proposal

Many of the problems with the clarity and applicability of the proposal stem from the attempt by the Agency to compress several petitions into one generic rule. This is in fact a proposal covering

AP00018795

polyesters and a variety of other low molecular weight products, most of which seem to be prepolymers and intermediates, not true polymeric products suitable for final processing or use. This would have been much clearer and effective if the proposal had been broken down into discrete classes of polymers based on application and structure/functionality, and not lumped together as they are. We recommend that the Agency rethink the organization of the proposal in order to make it more effective.

D. Molecular Weight Classes

Many structural polymers may have molecular weight as low as 6-8,000. The Nylons and low molecular weight polyethylenes are majors example of these. The physical state is a function of structure, size, and the interaction of polarizable segments. The 20,000 figure is not a parameter that is relatable to any basic principle. Empirical data suggest that a 5-6,000 cut-off is a more realistic division between materials that may or may not be able to enter the biosphere as other than inert substances. This is supported by the discussion at p. 33 at reference of Document 50, which describes polymers with molecular weights over 5,000 as physiologically inert. Whether or not the substance is "liquid" is not relevant. A material of molecular weight above 5,000 will not be a liquid in the ordinary sense. It may have some poor fluid properties, especially if heated, but certainly is not a conventional liquid, nor will it be water soluble unless a high ratio of polarizable groups is present. Petroleum waxes, such as those used in home canning, have molecular weights of only 400-700 (Kirk-Othmer loc. cit., Vol. 15, p. 93), and these have the least intermolecular interaction of any substance (there are no polar functional groups present) yet they are solids. Those with polar groups will be even less fluid.

Therefore we recommend 5,000, and not 20,000 as demarcation between low and high polymers.

E. Extraordinary Powers

The Agency grants to the Director of OTS extraordinary discretionary powers in proposal sec. 250 (n). Even after going to all of the extra effort to attempt to comply with the requirements of this proposal the producer has no assurance that the Director may not, for whatever reason, determine that "the manufacturer of the new chemical substance does not meet all of the terms of this section ---". There is no appeal, no hearing process, nor any other procedure for limiting the potential abuse of discretion under this section. We believe that this section is beyond the scope of the Act and the Administrative Procedures Act, and must be deleted or modified substantially before it is acceptable. Producers who enter into contracts as the result of an Agency action are subject to serious consequences if the Agency later rejects that action arbitrarily.

AP00018796

F. Functional Groups

The proposal at .250 (d)(3) and (b) that functional groups be limited to a ratio of 1 in 10,000 units is overly conservative and is inconsistent with current policy that allows a 2% by weight incorporation of a new monomer without a requirement of a PMN. Further, it is essentially impossible to meet in the class of polymers for which this proposal appears to be intended. A polymer of 5,000 molecular weight made from a monomer of 100 Daltons has only 50 units. Thus, this proposal would allow a functional group only once every 200 polymer molecules. This is an effective exclusion of functional groups, for they must be present in essentially all molecules to be useful.

It appears that this selection of 1 per 10,000 was a purely arbitrary choice. No support or rational is presented. The Agency should, therefore, withdraw that feature of the proposal and permit the current 2% rule to continue.

We support the conclusion that the functional groups listed in .250(d)(6)(ii) are safe and should be permitted.

G. Carbon Content

Proposed section .250(d)(2) would exclude polymers containing less than 32% carbon. The Preamble, at III.B.2, p. 33927 of the Notice states that this is because the Agency found no polymers with less carbon content in its PMN review. However, the support documents also state that the sample surveyed contained only 1% of examples containing halogen (document 54, p. IV-9) and that many subclasses of so-called "exotic" polymers were excluded from the final analysis.

The Agency has overlooked several major commercial families of polymers which have widespread applications in foods and health uses and in other important areas, which would be excluded if this proposal should be finalized. These include:

a) Fluorinated polymers such as polytetrafluoroethylene (24% C) or polychlorotrifluoroethylene (21% C) which are used in cookware, scientific instruments, medical implants, and nuclear energy.

b) Polymers containing vinylidene chloride (27-30% C) which are used in food packaging and many other home applications.

c) Chlorinated polyethylene and chlorinated PVC (about 28-30% C), which are used for domestic hot water piping and many industrial applications.

d) Glass (0% C), which is ubiquitous.

The arbitrary determination of 32% as a cut-off has no basis in health or scientific fact, and is derived from an incomplete and skewed sampling. It ignores the existence of major product

AP00018797

lines which would be excluded by its promulgation. There are no data presented suggesting that it would, in fact, offer protection from potentially hazardous solutions. This portion of the proposal should be withdrawn as ineffective and capricious.

VI. Risk Assessment

A. Vinyl Chloride

The quantitative risk assessment procedure used by the Agency in this Notice is extremely conservative. The risks projected are several orders of magnitude greater than the most probable actual risk. However, we agree with the Agency that when such a preliminary estimate shows no significant risk, there need be no concern, and the Agency need not undertake the more difficult task of preparing a realistic estimate. Such is the case for the risk from exposure to polymers.

However, when a preliminary risk estimate does give a result that is in the area of concern, the next step ought to be to reestimate the risk by sounder procedures. The Agency has not done this for the potential exposure to residual monomers, and has thus relied on estimated risks which are several orders of magnitude too high.

See our comments to companion Docket 50032A1 for a more detailed critique of the risk assessment methodology used here.

However, even without developing a more realistic reestimate for residual vinyl chloride, the Agency has made two serious errors in the risk calculation for that substance. Corrections of those errors will yield a risk estimate considerably below that which the Agency considers "significant".

1. Incorrect Potency Values

In Table 5, p. 43 of the Risk Analysis document (reference 47 of the Notice), the Agency presents in line 3 the risk estimates for two potencies (B-values), one for a value of 0.02, which is that calculated by the Agency for vinyl chloride itself, and another for a value of 2.0, based on a calculated value for acrylonitrile. Only the high level risk calculated from the assumed acrylonitrile value is noted as "significant". That for the vinyl chloride is below the significance level. Yet the Agency uses the acrylonitrile calculation to exclude vinyl chloride from the exemption process when it has a value for vinyl chloride itself which shows that the calculated risk is not significant.

The Agency is in error in using a value calculated for another substance when it has a value for the substance in question. Had the Agency used the proper value of B for the residual monomers from PVC, it would not have determined that vinyl chloride residuals were of concern. The Agency should, therefore, not include vinyl chloride as a monomer requiring exclusion from this proposed exemption process.

AP00018798

We would point out that the potency value of 2.0 for acrylonitrile is not that used by the Agency in the risk assessment document in Docket 50032A1, where the value of 0.37 was listed in Table A1, and is different still from the value actually given by the author cited as the source for Table A1. The Agency should explain this discrepancy in values, as well as its use of an incorrect value.

2. Incorrect Residual Monomer Levels

Further, in order to obtain the risk values which it did calculate, the Agency used, in Table 3, p. 41 of this document, a residual monomer value of 4%. The very limited data set which the Agency used in this exercise contained no materials in the molecular weight range of commercial PVC. See Table 2, p. 7, which shows a maximum M_n value of 50,000, whereas commercial PVC is above 60,000. Even so, the mean residual monomer value for the class of candidates with molecular weights above 10,000 was only 0.5%, not 4%.

In addition, the Agency should have known that it has a regulation, 40CFR61 (Subpart F), which prohibits the production of PVC with residual monomer greater than 400 ppm, or 0.04% in the slurry. The actual residual monomer level after separation from water and drying, when any significant exposure to the worker could occur, is substantially lower than that figure. See EPA 450/3-82-003, where it is shown that commercial product often is below 50 ppm. Thus, the projected risk is at least 100 times overstated by this error alone, and the value in Table 5 should be no more than 4.5×10^{-7}, under the conditions that may be used in the production of PVC.

We believe that the overall procedure used here is incorrect and that for vinyl chloride in particular is based on unsound methodology. See Barr, "Risk Assessment for Vinyl Chloride in Perspective", Paper 82-9.2, 75th Annual Meeting of the Air Pollution Control Association, New Orleans, June 20-25, 1982, copy attached, and our comments to Docket 50032A1. However, it is not necessary to open that argument in this matter, for the Agency data presented in the record of this proposal shows clearly that the Agency procedure does not calculate a significant risk for worker exposure to vinyl chloride when PVC is produced under the existing Agency regulation for its manufacture.

Therefore, the Agency should not exclude vinyl chloride-containing polymers from the exemption process based on an assumed risk to workers.

B. Water Soluble Polymers

The Agency has used the same worst case type of calculation to produce a postulated risk for water soluble polymers, without consideration of any specific material. We have shown above that

AP00018799

PVOH is not toxic by ingestion at low concentrations or from other modes of contact. Further, its usefulness as a soil conditioner (see Finch and Kirk-Othmer, loc. cits.) is based on the fact that it adheres strongly to soil particles. It is cross-linked and rendered insoluble by the multi-valent ions which are present in the soil. Thus, even if it were to be transported to the soil as a solution, it would be removed by the soil, and if it did reach an aquifer, no harm would come to those consuming that water.

We believe that the Agency should consider the actual risk of the specific polymeric structure, rather than regulating all materials after hypothesizing a risk based on worst-case conditions. Consideration of the data for PVOH will show that it poses no environmental risk because of its water solubility. The Agency should not base the risk assessment for PVOH on substances of totally different composition and properties, as it did in this matter.

We would note that other offices of the Agency, such as the Air Office, have encouraged the development and application of water soluble polymers. For example, these are used in the "solventless" surface coating applications because of their reduced impact on the environment as compared to solvent-based coatings. This proposal would be counterproductive to the effort by the Agency to reduce volatile organic emissions.

We also call attention to the discussion in the Notice document, p. 33 of document 50 of the record, which points out that polymers of molecular weight greater than 5,000 do not enter into biological systems. As we pointed out in Sec. III.1 above, PVOH has no physiological effects in animals, even when is introduced into the bloodstream at reasonable concentrations.

Paragraph .250(d)(6)(ii) of the proposal states that aliphatic hydroxyl groups are not of concern. This is the only functional group present in PVOH in any significant amount. Thus the Agency should have no concern for its presence, of the fact that it renders the product water soluble in some cases.

For these reasons, we believe it proper for the Agency to specify PVOH as a class of water soluble polymer not covered by the exclusion from the exemption.

C. Polymers Designed to Degrade

The risk assessment document makes no effort to develop a quantitative risk for degradable polymers, but merely assumes that they may produce a harmful product as they degrade (p. 70). The attached paper by Casey and Manley shows that PVOH is completely mineralized (goes to CO_2 and water) by biological degradation, and therefore will not produce toxic substances. The attached letter to a customer gives further experimental detail on the data heading to that conclusion. It does not revert to monomer on degradation, but if it did the monomer is not toxic. It does not form oligomers, but

AP00018800

is converted completely to harmless natural products. The data available to us indicates that the biological degradation does not proceed by internal chain scission, but by the conventional way, β-oxidation steps from the end of the chains.

Therefore, in the absence of evidence supporting its assumptions, and given evidence as to the safety of PVOH, the Agency should not rely on supposition to exclude PVOH from the exemptions proposed here.

VII. Improper Exclusionary Action

In view of the consistent low toxicity of and exposure to high molecular weight thermoplastics, such as PVC and PVOH, which are reported in the risk assessment document and the supporting mitre report, the Agency has taken a most unusual position as to their eligibility for the exclusion process proposed here. A major reason for that appears to be that this proposal is designed for an ill-defined group of low molecular weight prepolymers, and not for the greater class of structural polymers. Thus, this form of risk assessment is inappropriate for the PVC and PVOH families of polymers and ought not to be applied to them.

Another reason for the difficulties with this proposal may be that the Agency appears to have reversed the normal rulemaking procedures, and is proposing exemptions from a process that is not yet established by formal rule. Without firm information on the process for which the exemptions are being granted, we are unable to evaluate adequately the costs or benefits of the exemptions, and neither is the Agency, of course. We recognize the value of reducing the regulatory burden, that in order to appreciate that reduction it is necessary to have in hand a measure of the original burden. We do not have that now.

We urge the Agency to reconsider the potential hazards of these classes of substances and not to exclude them on the basis of assumptions not applicable to them. We see no evidence in the risk assessment document which points to any significant risk to humans or the environment from the manufacture or use of these classes of products.

VIII. Summary

In summary, we offer the following suggestions to the Agency on this proposal.

1. The Agency should make a clear statement that this proposal does not contemplate structural polymers, and then proceed to propose the elimination of structural polymers from the inventory requirements.

2. The Agency should reorganize the proposal into various classes of polyesters, prepolymers, and final polymers based on more suitable criteria.

3. The Agency should not provide a blanket exclusion for water soluble polymers, but should allow classes with suitable composition and functionality to be eligible for the proposed exemption.

AP00018801

4. The Agency should not exclude chlorine - containing polymers as a class without specific justification from consideration of the hazard of the particular polymer.

5. The Agency may not exclude classes of polymers from the exemption because of concerns for workplace or environmental exposure to the residual monomers because these effects are regulated by other statutes and regulations which the Agency is bound by Sec. 9 of the TSC Act to utilize first, should there be a hazard. Neither can the Agency use Sec. 5(4)(4) in place of the SNUR procedure.

6. The Agency has no basis in fact to exclude PVC or PVOH polymer classes from exemption under this proposal.

7. The economic analysis should be revised on the basis of realistic development costs for the required testing, and a more probable number of exemptions which may actually be sought. This proposal is unlikely to be used by any significant fraction of the producers of new polymers.

8. The polydispersity and molecular weight criteria which are proposed are arbitrary, and should be reestablished on the basis of scientific data.

9. The risk assessment is based on inappropriate assumptions and incorrect values, and should be withdrawn.

We support the basic concept of this proposal. Reduction of the burdens to industry and the Agency can provide considerable benefits to the public without an increase in risk.

The Agency has made a start at this program, but we believe that the suggestions outlined above will make the program more cost effective, and will place it on a much sounder scientific basis. This is needed, for it is our belief that the proposal, as presently stated, will not be useful to either the Agency or the regulated public, and thus will not achieve its stated goals.

AP00018802

ATTACHMENT I

POLYVINYL ALCOHOL BIODEGRADATION BY OXYGEN-ACTIVATED SLUDGE

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Summary

VINOL 325 Polyvinyl alcohol (PVOH) may be totally biodegraded as illustrated by controlled respirometric assays. Organisms which consume PVOH are viable in mixed culture activated sludges as determined by both synthetic and actual domestic wastewater studies in which PVOH was added to influent to a small scale multi-stage OASES correlation unit. Mixed culture growth rates analysed by appreciation of oxic solids residence time and clarifier damping factors permit sequential analyses of *Nitrosomonas*, *Nitrobacter*, and PVOH-degrading organism proliferation in activated sludge operated at successively lower dilution rates. A step increase in PVOH concentration allowed an initial calculation of PVOH organism growth rate within the oxygen activated sludge system of $\mu = 0{\cdot}34\ day^{-1}$ at $20 \pm 1°C$. A second scratch startup and examination of PVOH organism proliferation at a lower dilution rate confirmed this growth rate. Efficiencies of mixed culture PVOH degradation reached 13 mg PVOH/hr/g VSS with 3 hr influent residence time for a domestic wastewater primary clarifier effluent. Organisms degrading PVOH in mixed culture remained viable under H_2O_2 treatment conditions which were toxic to filamentous and nitrifying organisms. Systems removing >90% of 50 mg/litre PVOH, >95% of 40 mg/litre NH_3 and >90% of BOD_5 were operated with excellent macroscopic sludge properties.

DISCUSSION

In light of early documentation of microbial metabolism of PVOH to CO_2 and H_2O (Nord, 1936) and later reference thereto (Pritchard, 1970), it is surprising that aqueous solutions of PVOH were long accepted as minimally biodegradable. This conclusion has been affirmed by reports of 0·2% (Clemson, 1971) −1% (Burr, 1971) BOD/weight ratios determined by *Standard Methods* (APHA, 1971). The weakness of BOD testing to determine 'latent' biodegradability has been appreciated (Burr, 1971), yet other more rigorous methods have been employed to document the refractory nature of specific commercial PVOH products (Wirick, 1974).

Because of the extensive use of PVOH as a textile sizing agent and the need for nonpolluting textile wastewater treatment systems, considerable recent work on PVOH has appeared. A study reporting variable long-term BOD results for PVOH (Porter and Snider, 1974) protested the difficulty in relating controlled biodegradability tests to wastewater treatment operations. An integrated study of textile wastewater treatment technology dealt with activated sludge acclimatization to, and removal of, PVOH on a 2 litre scale (Bryan, 1972). A 20 litre and pilot scale study (Baines, 1973) documented

AP00018803

PVOH removal by activated sludge. Further work has generated dimensionless data proposing a loading ratio of 0·1 COD/MLSS and a solids aeration time (Sat) of 8 (g MLSS/L)(days) for efficient treatment (Hahn *et al.*, 1975).

Extensive work by Nippon Synthetic Chemical Industry Co., Ltd (Nishikawa and Fujita, 1975) has resulted in proprietary wastewater treatment technology claims involving additive and process control tactics, yet some textile plants have performed satisfactorily on an independent basis (Anon., 1974).

Clearer understanding of the fundamentals of PVOH microbial metabolism has been published (Suzuki *et al.*, 1973), but no satisfactory pure culture or mixed culture growth rate data are presently available. Such information is critical for application of bioengineering principles in wastewater treatment. The present study was undertaken to provide such information and develop

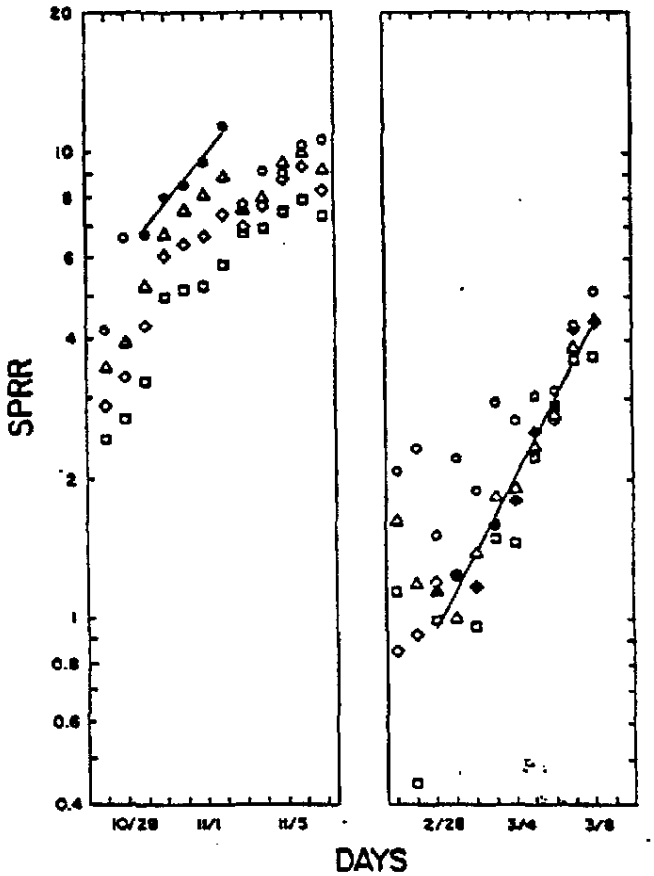

Fig. 1. Analyses of observed growth rate. ○ SPRR Stages 1–2; △ SPRR Stages 1–3; ◇ SPRR Stages 1–4; □ SPRR Stages 1–5. Filled symbols represent data for least squares line fit. Period I, slope 0·120 day⁻¹. Period II, slope 0·188 day⁻¹.

AP00018804

design criteria for treatment of wastewater containing polyvinyl alcohol.

Multiple-stage OASES correlation unit operation permitted stage by stage substrate determination on a daily grab sample basis. The interstage change in VINOL 325 concentration normalized to MLVSS level and stage residence time permitted calculation of a Specific PVOH Removal Rate (SPRR) expressed in mg PVOH/hr/g VSS. With the viable assumption that active mass degrading PVOH constituted a small fraction of the total MLVSS, the change in SPRR could be used to assay increased or decreased presence of PVOH-degrading bacteria. Given the assumption that SPRR is proportional to PVOH-active biomass (X), the expression $\mu = \int dX/dt/X$ to obtain the growth rate of active mass could be solved by obtaining the slope of *ln* SPRR plotted *vs.* days of operation.

Two summary periods of analysis are presented in Fig. 1. The volume-weighted averages of daily values of SPRR for multiple stages inclusive of the first were used for a least square line fit. Analysis of response to a step increase of VINOL 325 from 50 to 100 mg/litre during period I at constant flow rate results in an observed growth rate of 0·120 day^{-1}. Analysis of the increased rate of VINOL 325 degradation following trace seeding with supplemental active organisms during period II results in calculation of observed μ of 0·188 day^{-1}.

In each case the actual organism growth rate may be calculated after correction for the unit dilution rate, for the observed rates are reduced at higher system dilution rates. Furthermore, a factor which expresses the damping effect of clarifier inventory on observed system response is required. Given rigorous daily and summary average period data, this damping factor is easily calculable from reduction of a set of full system rate equations. Table I presents the specific data utilized to calculate actual growth rates $\mu = \mu_{dilu} + f\mu_{obs}$. These are 0·33 day^{-1} in response to the step increase in loading and 0·34 day^{-1} for response during the period of higher SRT. In mixed culture with activated sludge in the range of 19–22°C, the organism doubling time is therefore of the order of 2 days. Depending on the solids residence time of the chosen activated sludge system and the damping factor provided by ineffectual clarifier inventory, the time for doubling of observable organism presence may be substantially higher than the 5·8 or 3·7 days noted in the periods analysed above.

Table I

Period *Dates*	*I* 10/29–11/2	*II* 2/28–3/8
# days	5	9
μ_{obs} (day^{-1})	0·120	0·188
Correlation coefficient	0·989	0·973
MLVSS (mg/litre)	4 458 ± 290	4 482 ± 174
Aeration volume (L)	16	40
VSS produced/day (g)	12·4 ± 3·7	10·9 ± 5·3
SRT (day)	5·90	16·51
μ_{dilu} = 1/SRT (day^{-1})	0·170	0·060
f	1·353	1·468
$\mu_{dilu} + f\mu_{obs}$ (day^{-1})	0·333	0·338
T stage #1 (°C)	22·1 ± 0·3	20·3 ± 1·2
T last stage (°C)	21·0 ± 0·4	19·0 ± 1·4

AP00018805

This work demonstrates that definitive mixed culture growth rate data can be generated for organisms which biodegrade PVOH in mixed industrial-domestic wastewaters. Furthermore, the current scope of practicable bio-engineering technology (Landis *et al.*, 1974) can be utilized for the design and operation of activated sludge systems for PVOH removal.

MATERIALS AND METHODS

VINOL 325, degree of polymerization 1725 ± 25, degree of hydrolysis 98–99% and VINOL 540, degree of polymerization 2400 ± 50, degree of hydrolysis 87–89% were obtained from commercial lots produced at Air Products and Chemicals' Calvert City, Kentucky facility. PVOH-3 was obtained from a commercial lot imported for use as a textile sizing agent, and is a crotonic acid-vinyl alcohol co-polymer of medium viscosity and 94% degree of hydrolysis.

Suspended solids, BOD and COD measurements were performed following 'Standard Methods' (APHA, 1971). Nitrification of ammonia in the BOD test was supressed by addition of $1{\cdot}6 \times 10^{-4}$ M allylthiourea. Filtered BOD and COD data refer to filtrates obtained from aspirator vacuum filtration using 2·4 cm Reeve Angel glass fibre filter paper. BOD dissolved oxygen (DO) measurements, mixed liquor DO measurements, and dynamic oxygen uptake measurements were performed using a Yellow Springs Instrument stirred BOD probe model #54.

Ammonia, nitrite, nitrate plus nitrite, and hydrolysable phosphate determinations were performed on filtered samples using Technicon Autoanalyser II methods. VINOL concentration determinations using a boric acid-I_2/I_3^- procedure (Finley, 1961) were initially performed using a Perkin-Elmer Model 202 spectrophotometer, then automated for unit operations by adaptation to the Technicon Autoanalyzer II at 80 samples per hour using a 660 nm colourimetric filter for a full-scale range of 0–50 mg/litre VINOL 325.

Unit operations were performed using plexiglas aeration chambers in series. Submerged candle spargers supplied O_2/air/N_2 mixtures to the open-staged mixed liquor in which the gas pressures to each stage were separately reduced and gas flows were separately regulated and monitored by flow tubes. This gas system permitted simultaneous variation of desired DO levels and gas flows providing intrastage mixing at approximately 0·15–0·20 hp/1000 gal. Dynamic oxygen uptake measurements taken serially beginning with the final stage were facilitated by the independent gas flow controls, allowing dilution corrections of the form $dO_2/dt = (DO_t - DO_{t+1})/dt + (DO_{N-t} - (DO_t + DO_{t+1})/2)\,(Q/V)$ for the Nth stage upon terminating gas flow to that stage and providing mechanical stage mixing while recording the DO.

Domestic wastewater was obtained twice a week in epoxy-lined 55 gallon drums from the primary clarifier overflow at the Easton, Pa. sewage treatment plant. Desired concentrations of PVOH were obtained by addition of 5% PVOH concentrate to the barrels. Barrel contents were stirred mechanically to maintain influent solids suspension and were removed, using a Cole-Parmer positive displacement pump capable of drawing influent from the barrel bottom through a ¼ inch mesh wire screen protecting the tip of a ¼ inch ID plexiglas tube connected to tygon tubing on the pump suction side. Activated sludge recycled from the inclined cylindrical bottom of an 18 litre,

AP00018806

24 inch tall, 6 inch OD clarifier equipped with a 10 inch deep centrewell of 2 inches OD and sludge rake was introduced, via a second peristaltic pump, alongside the influent directly into the first aeration stage.

Daily data included determinations of DO, pH, temperature, TSS, VSS, $NH_3 - N$, $NO_2^- - N$, $NO_3^- + NO_2^- - N$, and PVOH for influent, effluent, and each aeration stage. The oxygen uptake rate (OUR), sludge volume index (SVI), and O_2/air/N_2 gas flows were recorded for each stage. A zone settling velocity (ZSV) and 30 minute stirred SVI (SSVI) were determined on the last stage mixed liquor in a 1 litre graduate using a 6 rph rake. Influent and effluent SS, BOD, and COD were determined at the beginning of the data day on grab samples and their filtrates obtained after overnight steady-stage operation. The Calcomp figures herein present 3-day running average data for daily values except for initial data days at new process conditions, which are represented by a 1-day and 2-day value, respectively.

RESULTS

VINOL 325 was first demonstrated to be nontoxic and noninhibitory upon short-term testing by addition to activated sludge organisms degrading a glucose-based synthetic wastewater. Response of 2500 mg/litre MLVSS from a state of endogenous oxygen uptake to a state of maximum oxygen uptake following addition of 1000 mg/litre glucose was unchanged upon addition of 400 mg/litre VINOL 325. A second indication of nontoxicity was obtained in seeded BOD tests using unacclimatized biomass. In tests of 5–20-day duration, the change in DO of the seeded BOD blanks was not substantially exceeded, but was equalled by, the change in DO (up to 4–5 mg/litre in some heavily seeded tests) of the BOD tests containing 3–7 mg/litre VINOL 325.

A survey of textile wastewater treatment plants was undertaken in parallel with initial acclimatization tests, and consisted of analytical work documenting PVOH removal by select plants, then collection of mixed liquor sludges capable of removing PVOH. A culture from one textile wastewater treatment plant in the Southeast was enriched in fill and draw tests to provide seed organisms to document PVOH biodegradation. Die-away analyses of VINOL 325 confirmed by COD analyses (COD/VINYL 325 = 1·64 g/g, theory ~1·82 g/g) indicated removal rates of 9–15 mg/hr/g VSS.

Supernatant from an endogenous mass of sludge acclimatized to PVOH was used as seed in a series of BOD tests performed without and with 3×10^{-5} M ATU to inhibit nitrification. In addition to replicate seed controls, each substrate was tested at 10, 15, and 30 × dilution of a 100 mg/litre stock solution. DO levels were monitored at 5-day increments through 30 days or until DO depletion, at which points PVOH, $NH_3 - N$, $NO_2^- - N$, and $NO_3^- + NO_2^- - N$ levels were monitored by Autoanalyzer II test methods.

Figure 2 presents summary plots of BOD data indicating levels of precision where multiple samples remained undepleted. Table II presents, based on stoichiometric oxygen consumptions for $NH_3 - N$ to $NO_2^- - N$; $NO_2^- - N$ to $NO_3^- - N$; and PVOH to CO_2 and H_2O, calculated and observed charges in DO levels. The agreement in nondepleted samples strongly suggests total oxidation of VINOL 325 and, after an initial lag, of the less fully hydrolysed VINOL 540. PVOH-3 proved substantially less degradable by the seed organisms acclimatized to VINOL 325.

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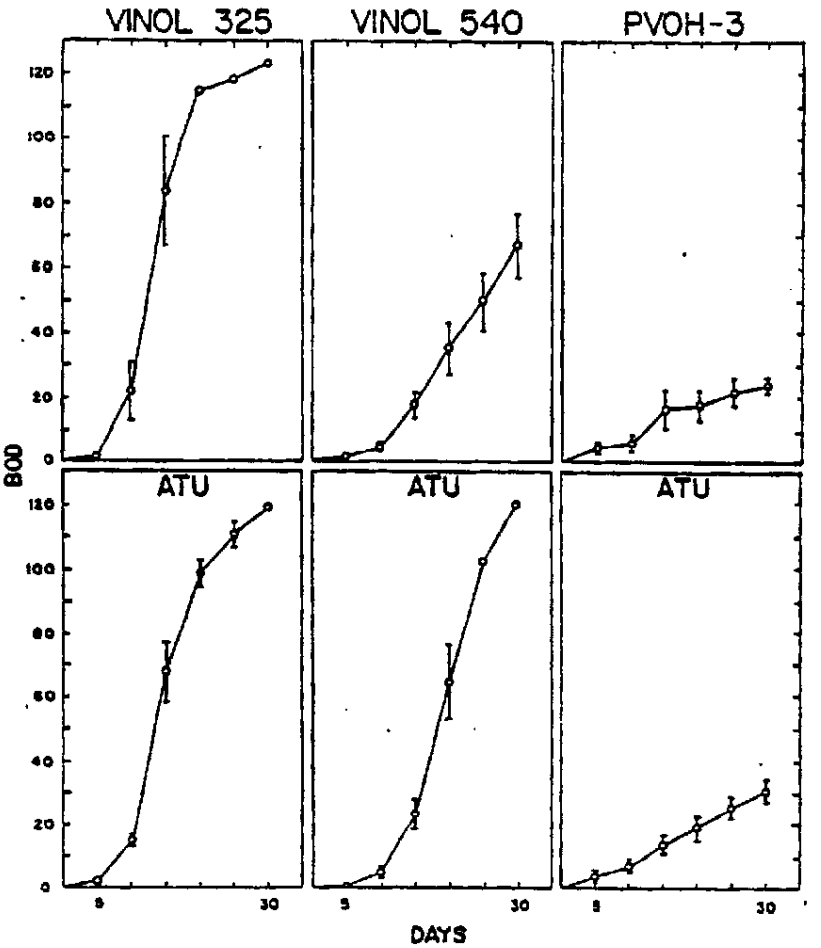

Fig. 2. Thirty day BOD tests without and with ATU inhibition of nitrification, corrected vs. corresponding blanks. I indicates Standard Deviation of nondepleted samples of varying dilutions of 100 mg/litre VINOL 325.

Table II
DISSOLVED OXYGEN BALANCES IN 30 DAY BIODEGRADATION OF 3·33 mg/litre PVOH

	$\Delta PVOH$	$\frac{\Delta DO}{PVOH}$	ΔNO_{3-}	$\frac{\Delta DO}{NO_{3-}}$	Calculated sum ΔDO	Actual sum ΔDO
VINOL 325	3·33	5·46	0·38	1·72	7·18	7·10
VINOL 325 with ATU	2·98	4·88	0·08	0·34	5·22	4·90
VINOL 540	1·58	2·61	0·46	2·08	4·69	5·25
VINOL 540 with ATU	3·33	5·49	0·06	0·26	5·75	4·90

AP00018808

Unit operations using a synthetic wastewater seeded with sludge enriched in PVOH acclimatized organisms followed successful initial fill and draw die-away analyses. Upon introduction of seed sludge to a stable synthetic wastewater unit operation unable to degrade PVOH, proliferations of filamentous organisms present in the seed sludge proved deleterious to unit operations. Following treatment of recycle sludge with 0·1 g H_2O_2/g TSS to oxidize filaments of *Sphaerotilus natans*, all nitrification within the system was suppressed, but PVOH removal capabilities remained.

Stable operations were then attained at low organic loadings employing a high degree of initial staging (Casey *et al.*, 1975). Nitrification plus VINOL 325 removal capabilities of activated sludge were examined for synthetic wastewater supplemented with VINOL 325, for a synthetic waste consisting solely of VINOL 325 as a carbon source, then for a domestic wastewater supplemented with VINOL 325.

Data for unit operations from 10/16/73–3/20/74 have been selected for review, and are presented in Figs. 3–12. A chronology is presented in Table III

Table III
SUMMARY CHRONOLOGY

Date	
10/26[a]	One day removal of PVOH from influent
10/30[a]	Step increase in VINOL 325 from 50–100 mg/litre
11/3[a]	Increased flow
11/21[a]	New unacclimatized unit operation
12/1[a]	Decrease VINOL 325 from 100 to 50 mg/litre
12/5	Auxiliary unit operation studies
1/3[a]	Increase five stages of aeration volume by 50%
1/14[a]	Increase aeration volume by 67%, to seven stages
2/1[a]	Increase flow to build solids level
2/13[a]	Decrease flow
2/26	Addition of 100 mg/litre alkalinity to influent
2/28	Seed sludge addition, 5% of inventory
3/14	Omit VINOL 325 addition
3/21	Alternative unit operation studies

[a] Major process changes, figures restart 3-day running average.

for data from a previously initiated unit operation and operation reflecting performance of sludge produced in an OASES correlation unit not previously exposed to PVOH.

At 4 hr influent detection time for a five stage 16-litre unit, operation with 33% sludge recycle resulted in 3 hr nominal residence time (Fig. 3). Easton wastewater of moderate strength contained 520 mg/litre COD (Fig. 4) and 120 mg/litre BOD_5 (Fig. 5). The COD included a contribution of 80–90 mg/litre from VINOL 325 supplement, but the BOD_5 did not reflect VINOL 325 presence as the influent 5-day BOD tests were run without seed. With a nominal 6000 mg/litre MLSS, 4800 mg/litre MLVSS (Fig. 6) under aeration with stable sludge properties (SVI of 60 ml/g TSS and ZSV of 6 ft/hr), removal of 35 mg/litre ammonia was complete by nitrification to $NO_3^- + NO_2^- - N$ (Fig. 7). Removal of 60 mg/litre VINOL 325 was also complete (Fig. 8).

Following 10/25 data, the fresh daily domestic wastewater influent was not supplemented with VINOL 325. The 24-hr absence of substrate had substantially no effect upon overall removal efficiency upon re-addition jo VINOL 325 the following day.

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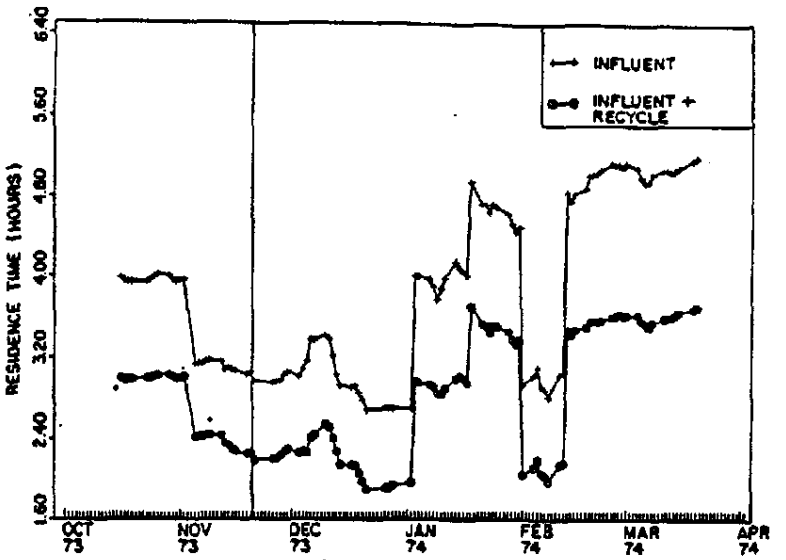

Fig. 3. Domestic wastewater detention time in OASES correlation unit.

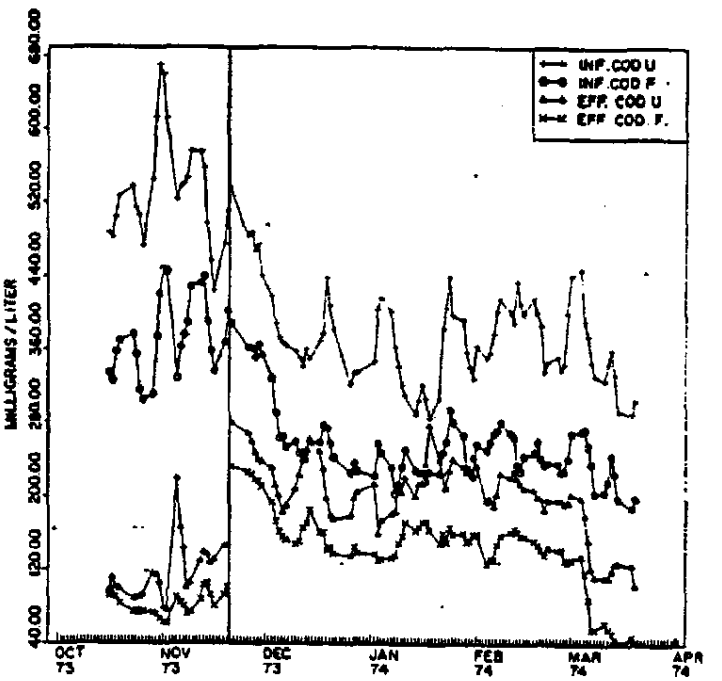

Fig. 4. Domestic wastewater unfiltered (U) and filtered (F) COD values.

AP00018810

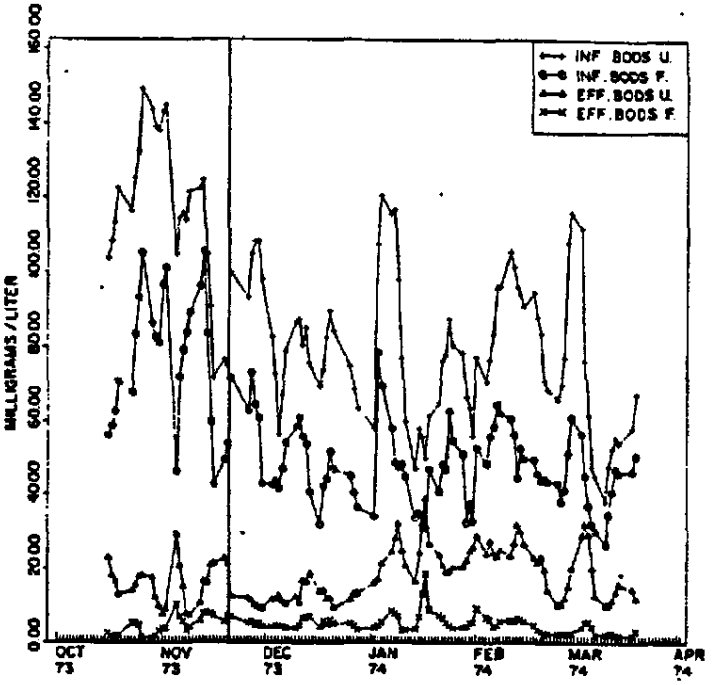

Fig. 5. Domestic wastewater unfiltered (U) and filtered (F) BOD_5 values.

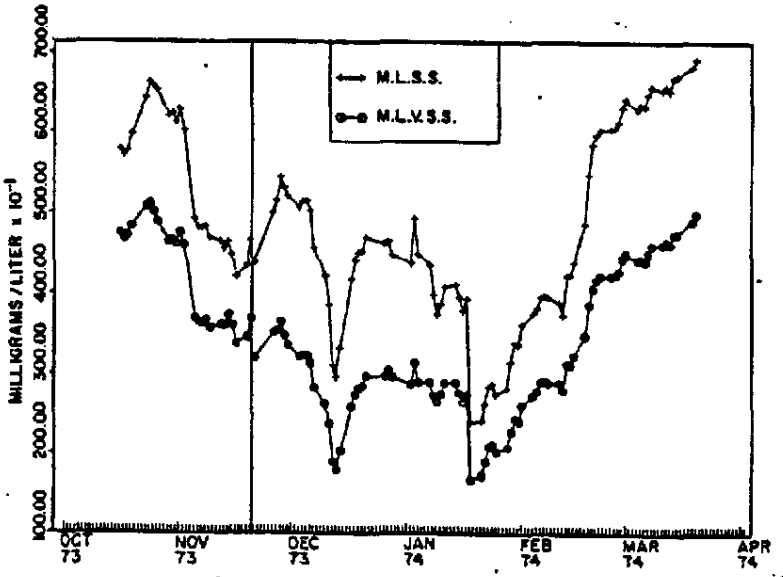

Fig. 6. Mixed liquor total and volatile suspended solids.

AP00018811

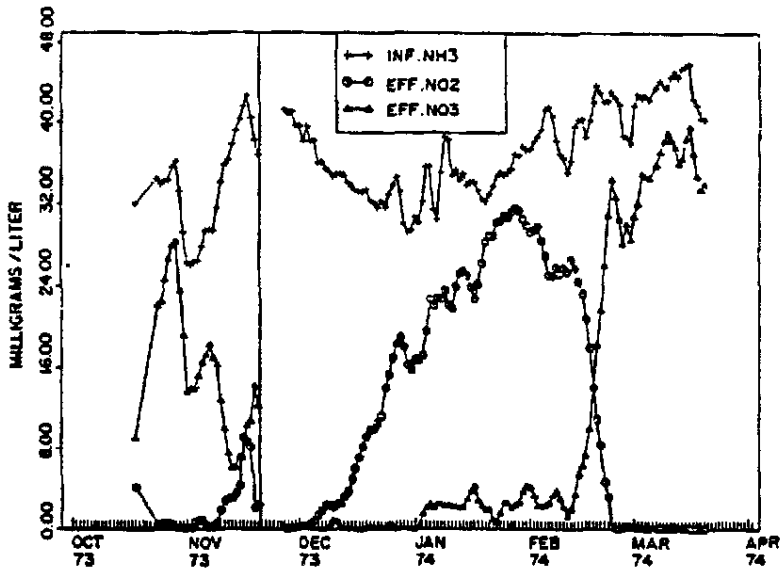

Fig. 7. Domestic wastewater ammonia and oxidation thereof.

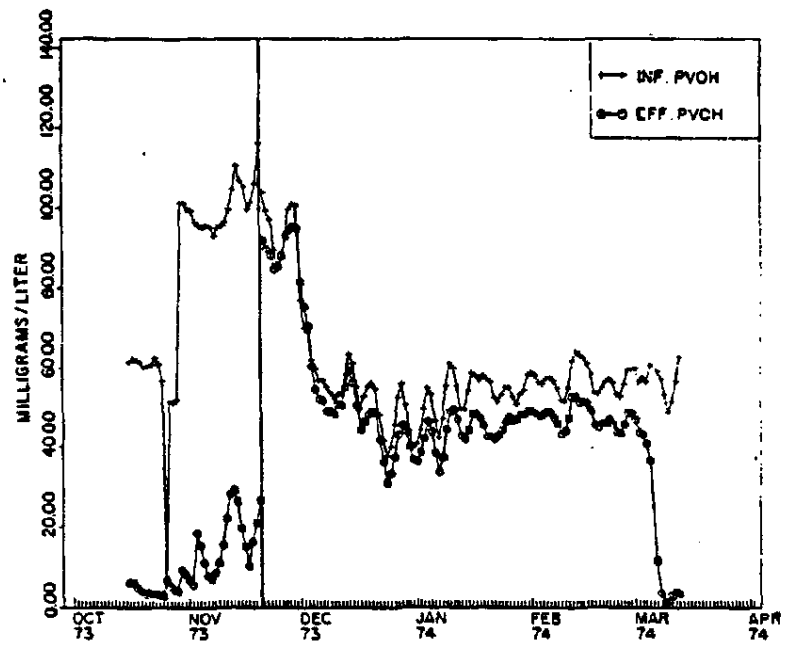

Fig. 8. Domestic wastewater VINOL 325 supplement.

AP00018812

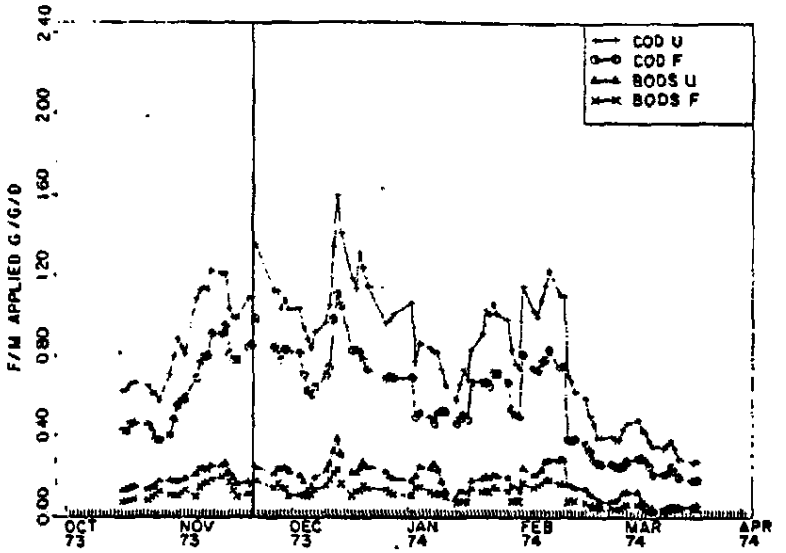

Fig. 9. Domestic wastewater organic loading.

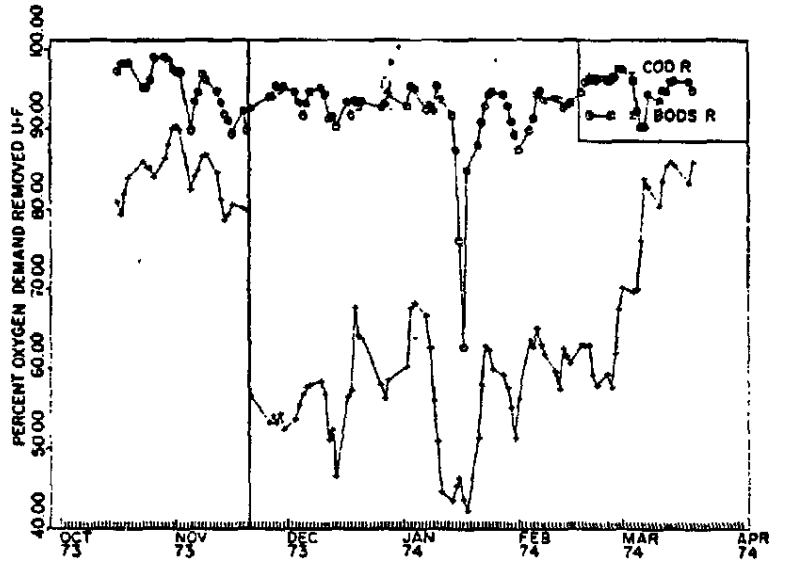

Fig. 10. Domestic wastewater COD and BOD_5 removal efficiency.

AP00018813

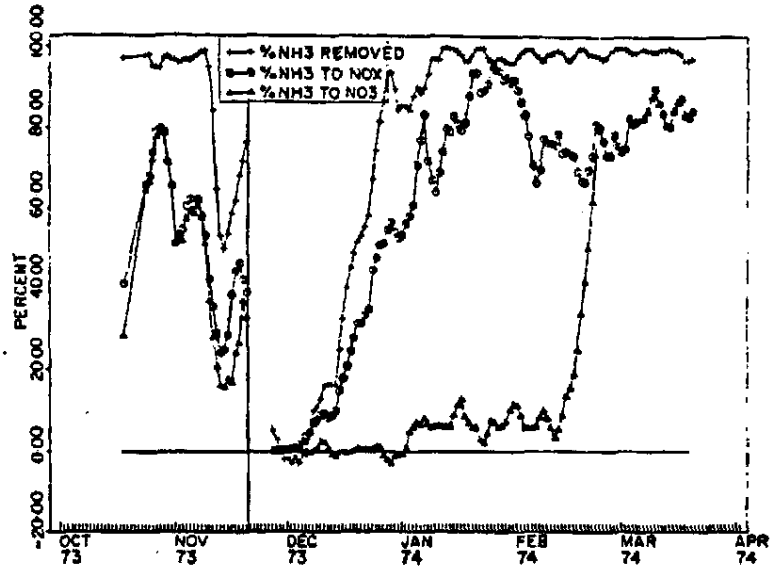

Fig. 11. Domestic wastewater nitrification efficiency.

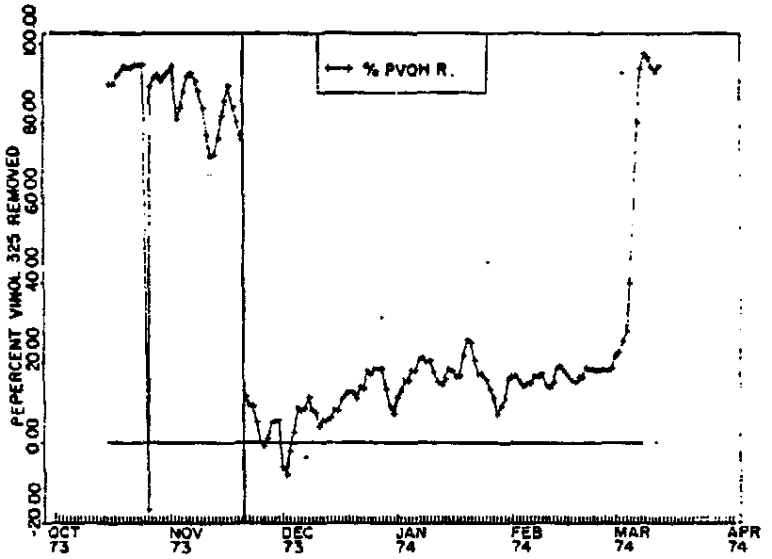

Fig. 12. Domestic wastewater VINOL 325 removal efficiency.

AP00018814

Following 10/29 data, the VINOL 325 concentration was doubled to 100 mg/litre. Significantly, overall removal efficiency was maintained and PVOH removal remained above 90% and COD removal above 85%.

Following 11/2 data, the influent and recycle flows were increased by approximately 30% to give a influent detection time of 3·2 hr and nominal residence time of 2·4 hr. VINOL 325 concentration rose initially to 18 mg/litre, but was then reduced daily despite the higher flow conditions. With slightly increased flow and lower MLVSS levels resulting from greater hydraulic throughput in the clarifier, hence less dense underflow despite essentially similar macroscopic sludge properties, the unit operation proved sensitive to changes in influent strength over the next period of operation from 11/9–11/20. This F/M (Fig. 9) sensitivity showed parallel responses of OD removal, nitrification, and PVOH removal efficiencies (Figs. 10–12), for as influent strength increased, then decreased, % ammonia removal, % nitrification, and % VINOL 325 removal decreased, then increased. These operations demonstrated borderline conditions for system efficiency.

To ascertain conditions necessary to commence stable PVOH removal, a parallel unit operation which had not been exposed to VINOL 325 and which had a history of 7–9°C activated sludge operation was dedicated to continuing VINOL 325 studies at 20°C. Beginning 11/21 at control conditions identical to the former operation, VINOL 325 was added to domestic substrate at 100 mg/litre. Reductions of VINOL 325 of 12–8 mg/litre during the first 3 days of operation were followed by a period of essentially zero reduction through the next week, after which time the influent VINOL 325 was reduced to 50 mg/litre.

Over the next month, during a period of auxiliary investigations, the VINOL 325 removal increased slowly to 8–10 mg/litre, representing 15–20% overall removal efficiency. Following the Christmas/New Year hiatus in full data collection, expansion of the aeration volume from 16 to 24 litres to give five liquid stages at 8 inches liquid height of 2·4, 4·8, 4·8, 4·8, and 7·2 litres was undertaken after data on 1/2.

Operations continued at 4·0 hr influent detection time with 33% sludge recycle to give 3·0 hr nominal residence time through 1/17, encompassing a period of low influent strength, total nitrification to nitrite, and rather steady removal of 8–10 mg/litre VINOL 325.

After 1/17 data, two 8-litre stages were added to give a total aeration volume of 40 litres composed of seven stages. Dilution of the aeration plus clarifier inventory resulted in an MLVSS level of ~1700 mg/litre. At this low solids level sludge settling rates approached 15 ft/hr, resulting in increased weir losses from too rapid a settling rate in the clarifier. Over a 12-day period with only sampling losses constituting sludge wasting, the VSS produced per day of 13·8 g resulted in an inventory increase of only 3·4 g/day due to weir losses of 9·0 g/day in addition to the minimal wasting of 1·4 g/day.

To effect an increase in system inventory yet attain solids residence time control through daily wasting, the influent flow was increased by 50% and the percentage sludge recycle was increased from 33 to 40% of influent flow.

After reaching >3000 mg/litre MLVSS with controlled daily wasting on 2/12, the influent and recycle were reduced to give an influent detention time of 5·0 hr and nominal residence time of 3·6 hr from 40% sludge recycle. These conditions were maintained at 19–22°C through the following weeks of controlled wasting to obtain MLVSS level increases to 4000, 4500, 4750, and 5000 mg/litre, respectively.

AP00018815

Nitrification to nitrate increased at a rapid rate from 2/13–25, at which point some reduction in ammonia removal rate for the moderate strength (100 ml/l BOD_5), high ammonia (40 mg/l $NH_3 - N$) wastewater was noted due to alkalinity losses caused by nitrate pH depression in the terminal aeration stages. Addition of sodium bicarbonate to the influent equal to 100 mg/litre alkalinity as $CaCO_3$ was instituted 2/26 and eliminated the ammonia breakthrough.

VINOL 325 removal of 10–12 mg/litre was constant during operation through 2/27, at which time previously wasted sludge acclimatized to VINOL 325 in fill and draw tests was seeded at 5% of total inventory (12·6 g VSS to 265·3 g VSS) into the unit operation. At relatively constant influent strength applied to 4500 mg/litre MLVSS, the PVOH removal levels were 11, 16, 12, 16, and 16 mg/litre VINOL 325 for sequential days during which sludge production averaged near the prior period norm of 12 g/day. On the following 3 days of operation, the next biweekly influent wastewater shipment was applied. PVOH removal increased to 37, 49, and 55 mg/litre as influent BOD dropped from the previous shipment value of ~100 mg/litre to ~40 mg/litre and daily sludge production was approximately halved. VINOL 325 removal was maintained at greater than 90% of a nominal influent concentration of 50 mg/litre for one week, then unit operation parameters were maintained with the exception that VINOL 325 was removed from the influent.

REFERENCES

Anon. (1974). Blair's trained bugs eat PVA waste. *Textile World*, February 1974, p. 43.

APHA, AWWA, WPCF (1971). Standard Methods for the Examination of Water and Wastewater, 13th Ed., APHA, Washington, D.C.

Baines, F. C. (1973). Biodegradation of Polyvinyl Alcohol, AATCC Symposium, *The Textile Industry and the Environment*, May 22–24, 1973.

Bryan, C. E. (1972). Dept. of Textile Chemistry, School of Textiles, North Carolina State Univ., Water Pollution Reduction Through Recovery of Desizing Wastes. *U.S. EPA Clean Water, Water Pollut. Control Res. Ser.* 12060 EOE 01/72.

Burr, F. K. (1971). Textile waste treatment. In *Textile Technology, Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Edn. Supplement Volume. J. Wiley & Sons, Interscience, New York. 980 pp.

Casey, J. P., McDowell, C. S., Spector, M. L., and Zupko, A. J. (1975). Non Bulking Activated Sludge Process. U.S. Patent 3,864,246 assigned to Air Products and Chemicals, Inc., 4 February 1975.

Clemson University Department of Textiles (1971). State-of-the-Art of Textile Waste Treatment, A Study Conducted for the Water Quality Office of the EPA, Grant No. 12090 ECS.

Finley, J. D. (1961). Spectrophotometric determination of polyvinyl alcohol in paper coatings. *Anal. Chem.*, 33, 1925.

Hahn, W. C., Barnhart, E. L., and Meighan, R. B. (1975). The Biodegradability of Synthetic Size Material Used in Textile Processing. 30th Annual Purdue Industrial Waste Conference, Purdue Univ., West Lafayette, Indiana, May 6–8, 1975.

Landis, J. G., Casey, J. P., and Hartzog, D. G. (1974). Oxygen Activated Sludge: Design by Waste Analysis and Modelling. 47th Annual WPCF Conference, October 6–11, 1974.

Nishikawa, H., and Fujita, Y. (1975). Polyvinyl Alcohol Degradation Techniques Using Microorganisms. *Chem. Economy Eng. Rev.*, 7, 33.

Nord, F. F. (1936). *Naturwiss*, 24, 763.

AP00018816

Porter, J. J., and Snider, E. H. (1974). Long-Term Biodegradability of Textile Chemicals. Third Annual Clemson Univ. Textile Pollution Control Conference, January 23–25, 1974.

Pritchard, J. G. (1970). *Poly(vinyl alcohol), Basic Properties and Uses.* Gordon and Breach, London. 117 pp.

Suzuki, T., Yoshihiro, I., Yamada, M., and Tonomura, K. (1973). Some characteristics of *Pseudomonas* O-3 which utilizes polyvinyl alcohol. *Agr. Biol. Chem.*, 37, 747.

Wirick, M. G. (1974). Aerobic biodegradation of carboxymethyl cellulose. *J. Water Pollut. Control Fed.*, 46, 512.

AP00018817

PROCEEDINGS OF THE THIRD INTERNATIONAL BIODEGRADATION SYMPOSIUM

Editors

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and

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ATTACHMENT II

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Industrial Chemicals Technology
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Telex: 847415

April 1, 1982

Dear

Enclosed for your use are graphs and tables which demonstrate efficient biodegradation of Etowah influent by biomass from the Springs Mills textile wastewater treatment facility. Also presented are respirometry data for both VINOL 205 and VINOL 325 which show equivalent biooxidation for the polyvinyl alcohol you will be using for fiberglass sizing and that previously discussed in APCI technical literature on activated sludge. I think these data provide sufficient positive information to approach the Federal and State people for permitting, for the biomass used in these respirometry tests will be available for full-scale plant start-up.

The Etowah activated sludge plant has four stages, each at 5000 gallons with a 7.5 horsepower submerged turbine. The airflow is specified at 1500 scfm to treat 100,000 gallons/day of influent at about 1000 mg/l weight alcohol in open tanks. The process option of oxygen use in closed tanks has not been eliminated from future consideration.

The bench scale simulation of the Etowah biotreatment technology now being conducted at ERG has recently been seeded with Springs Mills biomass known to biodegrade polyvinyl alcohol and should perform satisfactorily with these adapted bacteria. The commercial benchtop unit has a single aeration stage and an internal settling zone. It is being 'fed' influent at 90% - 1000 mg/l VINOL 205 / 10% sanitary wastewater composited by ERG dilution from a 1% VINOL 205 waste concentrate.

When we met with Peter Collins and Bruce Bartley of ERG in Ann Arbor on March 24 I recommended an increase in intensity of their study:

- Monitor the biomass inventory daily to judge activated sludge biomass growth based on solids produced = wasting + inventory change + effluent losses - influent suspended solids.

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- o Measure nutrient influent and effluent levels as NH3-N and PO4-P to assure a 100:5:1 BOD:N:P ratio. Approximate stoichiometry for PVOH is
  TOC/WT = 24/44 = .5455
  COD/WT = 80/44 = 1.82
  COD/TOC = 80/24 = 3.33
  BOD/COD = 2/3
  BOD/WT = 1.21
  BOD/TOC = 2.22

- o Obtain daily COD data to evaluate unit operations. The filtration of influent and effluent through glass fiber fiter paper provides a proper filtrate for soluble COD analysis.

- o Obtain TOC data, requiring smaller sample size, to monitor the COD/TOC ratio as an indicator of substrate change.

We agreed a quick APCI lab study using biomass and Etowah influent might provide site-specific feasibility data of immediate use. The appended electrolytic respirometry data were taken using an array of Oceanography International cells. Data were processed through mini- and mainframe computers to generate the graphs. The summary tables itemize key data on initial and final cell contents and the critical values of percent TOC removed and O2/TOC. For the first run we added the influent as received from ERG to get the cells up on Friday, 26 March. We analyzed the biomass TSS at 5000 mg/l and diluted to give 250 mg/l TSS in the cells.

Since the initial chain scission of PVOH is performed by extracellular enzymes we ran the control of endogenous respiration versus two levels of ERG/Etowah influent with washed biomass as well as with the biomass as received. The washed cells are slower to exhibit significant oxygen consumption on the lower levels of initial TOC. By subtracting the oxygen uptake for cell 1 from that of 2 and 3, and doing the same for cells 4-6 a clear normalization is available and is used in the subsequent plots of rates of O2 use per unit time. The final plot of the log(rate) data is to obtain a linear least squares fit approximating the bacterial growth rate. The plots for PVOH-1 are a bit noisy due to the low substrate levels, but show a growth rate averaging .0188/hr, or .45/day, suggesting that at 25 degrees C, the temperature of the respirometer runs, an aerobic solids residence time of 1/.45 = 2.2 days should lead to retention of these PVOH-degrading bacteria.

Qualitatively, then, the respirometry indicates a 'go' for Etowah biodegradation. Quantitatively, the TOC removal is 79% (cell 3) to 94% (cell 6) and the O2/TOC = 2.71 g/g (average of 2,3,5,6).

Because the run set up on 3/26 was essentially over on 3/29 due to substrate limitations, we continued the study by removing aliquots

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from each cell for analyses and adding VINOL 205 and VINOL 325 to the cells as indicated. I interpret the faster O2 takeoff in PVOH-2 for cells 3 and 6 as due to their higher prior level of substrate as much as due to any real difference in the biodegradability of VINOL 205 versus that of VINOL 325. The very close log(rate) data plots in the final presentations for PVOH-2, showing growth rates of .0168 and .0182/hr for VINOL 205 and .0186 and .0157/hr for VINOL 325, indicate no significant differences in biooxidizability.

The summary data in the table for PVOH-2 document TOC removal of 94% to 96% in all cells and an O2/TOC ratio of 2.12 for VINOL 205 and 2.27 for VINOL 325.

At higher substrate levels the test data for PVOH-2 are the better values to use for extrapolations to design, thereby indicating an average growth rate of .0174/hr and suggesting an aerobic solids residence time or 'sludge age' of but 2.4 days will maintain these PVOH-degrading bacteria in the system.

Based on the maximum final solids level of 450 mg/l TSS in cell 2 and the O2 consumption rates of 6-7 mg/l/hour in PVOH-2, the specific oxygen consumption rate in these tests is at least 14 mg/hr/gram TSS. Since the O2/TOC ratio is 2.2 for PVOH-2 and the TOC/WT is .546 for the VINOLs the rate of PVOH removal is 14 mg O2/hr/g TSS * TOC/2.2 O2 * PVOH/ .546 TOC = 12 mg PVOH/hr/g TSS. With a 4 hour detention time and 5 g TSS/l the PVOH removal ability of the bench scale unit, with this active a biomass, is about 240 mg/l PVOH. To remove 1000 mg/l PVOH a more active biomass or longer residence time is needed. The quickest way to optimze biomass activity is to increase the growth of the desired PVOH-degrading bacteria by operating at optimum growth rate conditions, say 33-37 degrees C. The above capacity analysis is a conservative evaluation that VINOL biotreatability is assured, but that operational success is going to be dependent on upgrading the activity of the seed biomass given the current detention time constraints.

Please contact me through our polymer technology staff if I can be of further help.

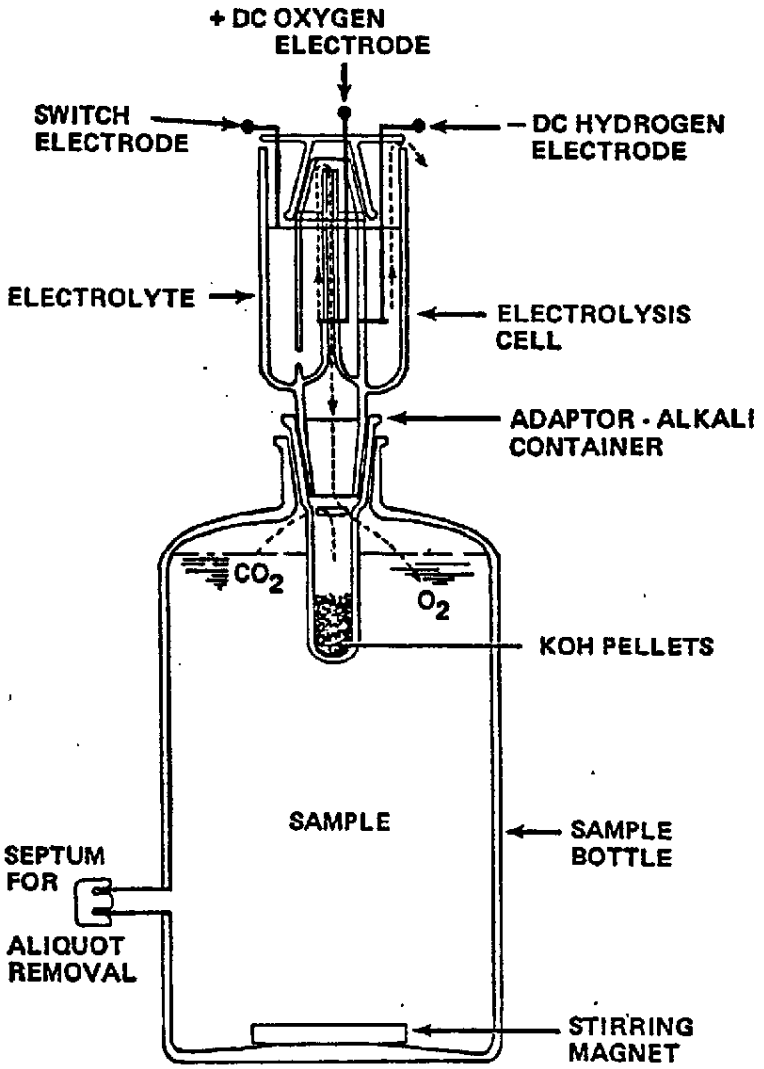
Sincerely yours;

Jeremiah

J.P.Casey
Research Chemist

c.c. B.Bartley
P.Collins
L.Newman
D.Stowe

Attachments:
Figure .. 1
Tables .. 2
Plots ...11
J/j



SCHEMATIC DIAGRAM SHOWING THE BASIC OPERATION OF THE ELECTROLYSIS SYSTEM FOR MEASURING BOD

AP00018822

RESPIROMETER RUN PVOH-1

Cell #	1	2	3	4	5	6
SEED	----250 MG/L TSS ERG-SPRINGS MILLS BIOMASS----					
	/----washed cells----/			/---unwashed cells---/		
SUBSTRATE	Control	Etowah Influent	Etowah Influent	Control	Etowah Influent	Etowah Influent
INITIAL*						
pH	6.99	6.95	6.94	6.96	6.92	6.97
TOC (mg/l)	12.0	14.6	32.1	27.5	31.9	53.1
TSS	267	285	298	286	276	281
VSS	208	236	222	232	226	223
%VSS	77.9	82.8	74.5	81.1	81.9	79.4
FINAL						
pH	7.01	6.90	6.91	6.89	6.84	6.90
TOC	11.2	11.5	15.4	13.5	14.4	15.1
Δ(68 hrs)						
O2	53.3	58.3	104	86.3	98.4	135
TOC	.8	3.1	16.7	14.0	17.5	38.0
%TOC Red'n	6.7	21.2	52.0	50.9	54.9	71.6
O2/TOC	7.95	18.8	6.28	6.16	5.62	3.55
ΔΔ						
O2		5.0	50.7		12.1	48.7
TOC		2.3	15.9		3.5	24.0
%TOC Red'n		88.5	79.1		79.5	93.8
O2/TOC		2.17	3.19		3.46	2.03

*Made up with BOD nutrients, PO4 buffer with NH4Cl to give 28 ppm N per cell in 2,5 and twice that level in 3,6; titrated to pH 7 with H3PO4, 20 mg/l allylthiourea added to inhibit nitrification.

Etowah influent composed of 90% VINOL 205 wastewater and 10% sanitary effluent; measured TOC of material received from ERG = 576 mg/l.
Seed biomass received from Springs Mills/ERG = 5034 TSS, 4476 VSS.

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NB 7018:51-54

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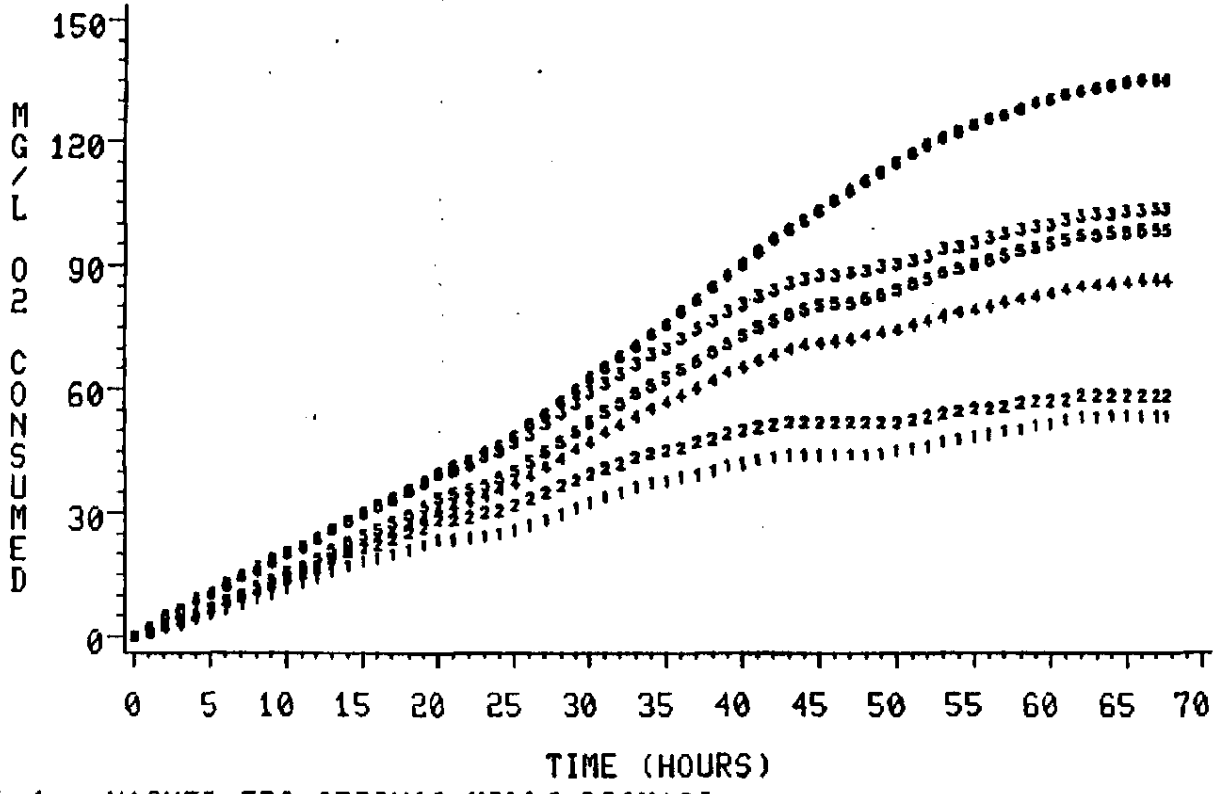
ELECTROLYTIC RESPIROMETER RUN PVOH-1



CELL 1 - WASHED ERG/SPRINGS MILLS BIOMASS
CELL 2 - 1 W 10 MG/L WT ETOWAH INFLUENT
CELL 3 - 1 W 50 MG/L INFLUENT-90% V205
CELL 4 - UNWASHED ERG/SPRINGS MILLS BIOMASS
CELL 5 - 4 W 10 MG/L WT ETOWAH INFLUENT
CELL 6 - 4 W 50 MG/L INFLUENT-90% V205

RUNDATE 032682-032982
REF BJK NB 7018:51-54

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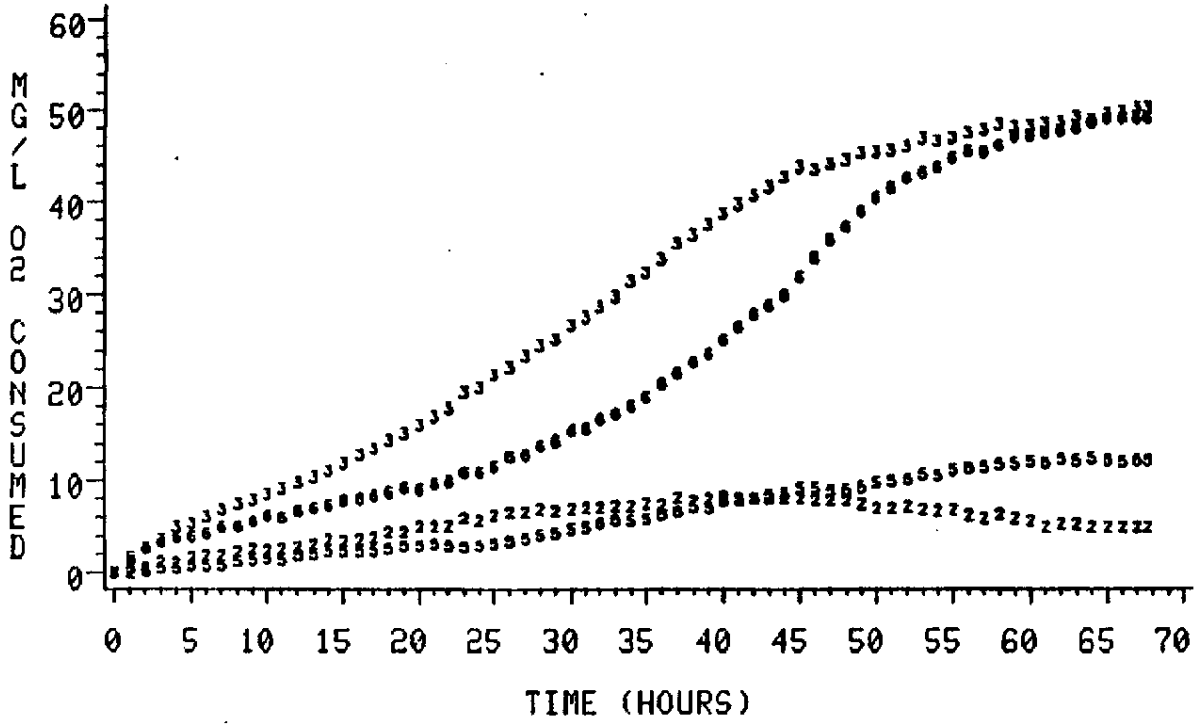
ELECTROLYTIC RESPIROMETER RUN PVOH-1



CELLS 2,3 - RESPIRATION OF WASHED ERG/SPRINGS MILLS
. BIOMASS CORRECTED FOR CONTROL CELL BIOMASS...
. ALLYLTHIOUREA ADDED FOR NITRIFICATION INHIBITION
CELLS 5,6 - RESPIRATION OF UNWASHED BIOMASS CORRECTED
. FOR CONTROL CELL BIOMASS ENDOGENOUS RATE RUNDATE 032682-032982
. AS ABOVE, NUTRIENTS ADDED FOR TEST ON TWO
. LEVELS OF ETOWAH INFLUENT..10, 50 MG/L BY WT REF BJK NB 7018:51-54

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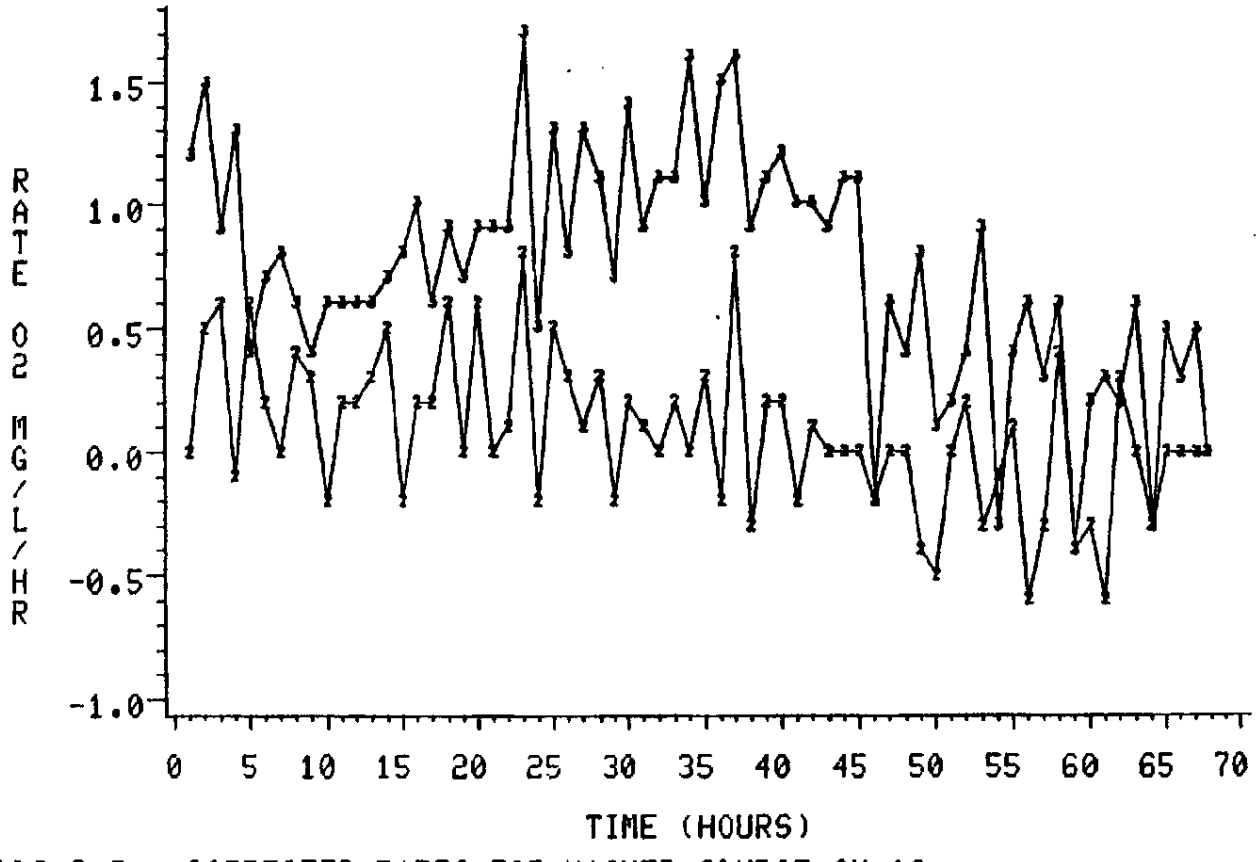

CELLS 2.3 - CORRECTED RATES FOR WASHED SLUDGE ON 10,
50 MG/L ETOWAH INF..90% V205-10% SANITARY

RUNDATE 032682-032982
REF BJK NB 7018:51-54

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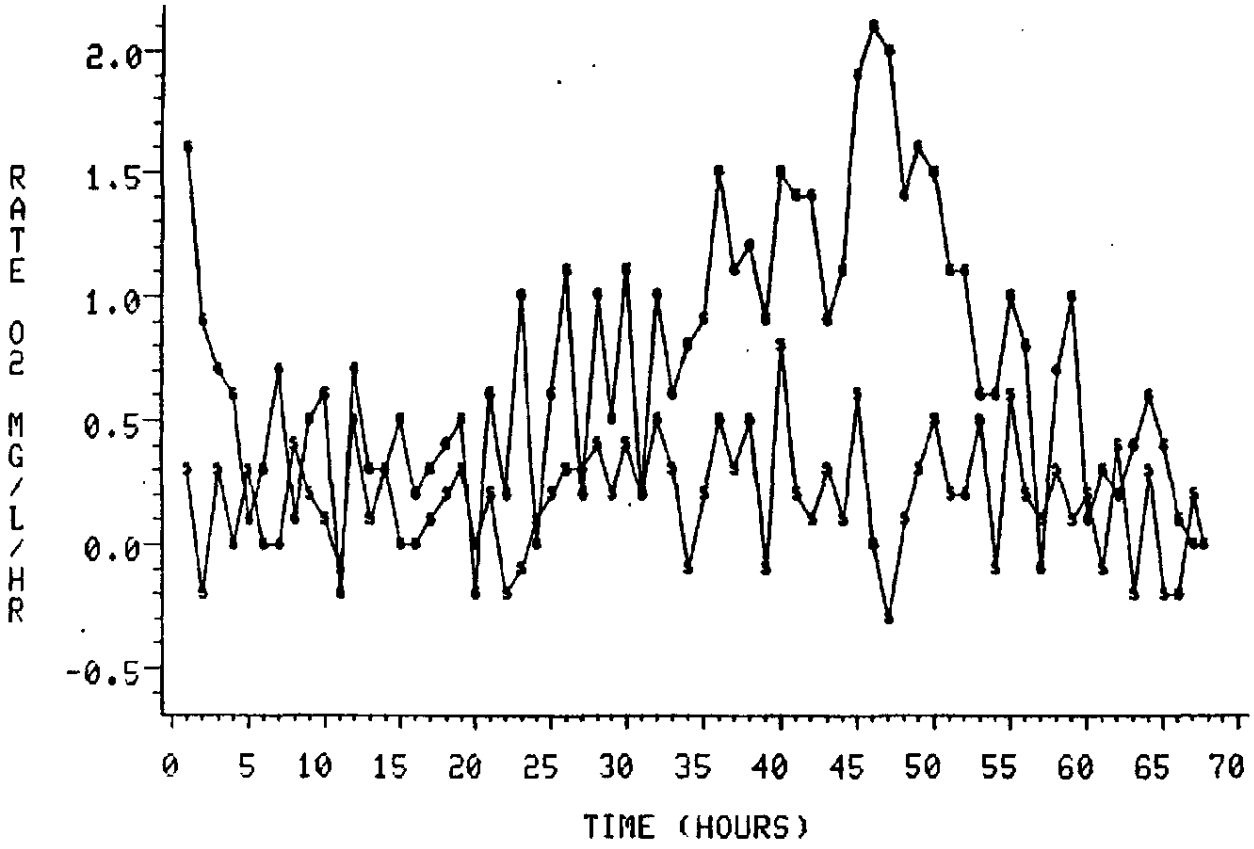
RESPIROMETER RUN PVOH-1



CELLS 5,6 - CORRECTED RATES FOR WASHED SLUDGE ON 10,
. 50 MG/L ETOWAH INF..90% V205-10% SANITARY
.
.

RUNDATE 032682-032982
REF BJK NB 7018:51-54

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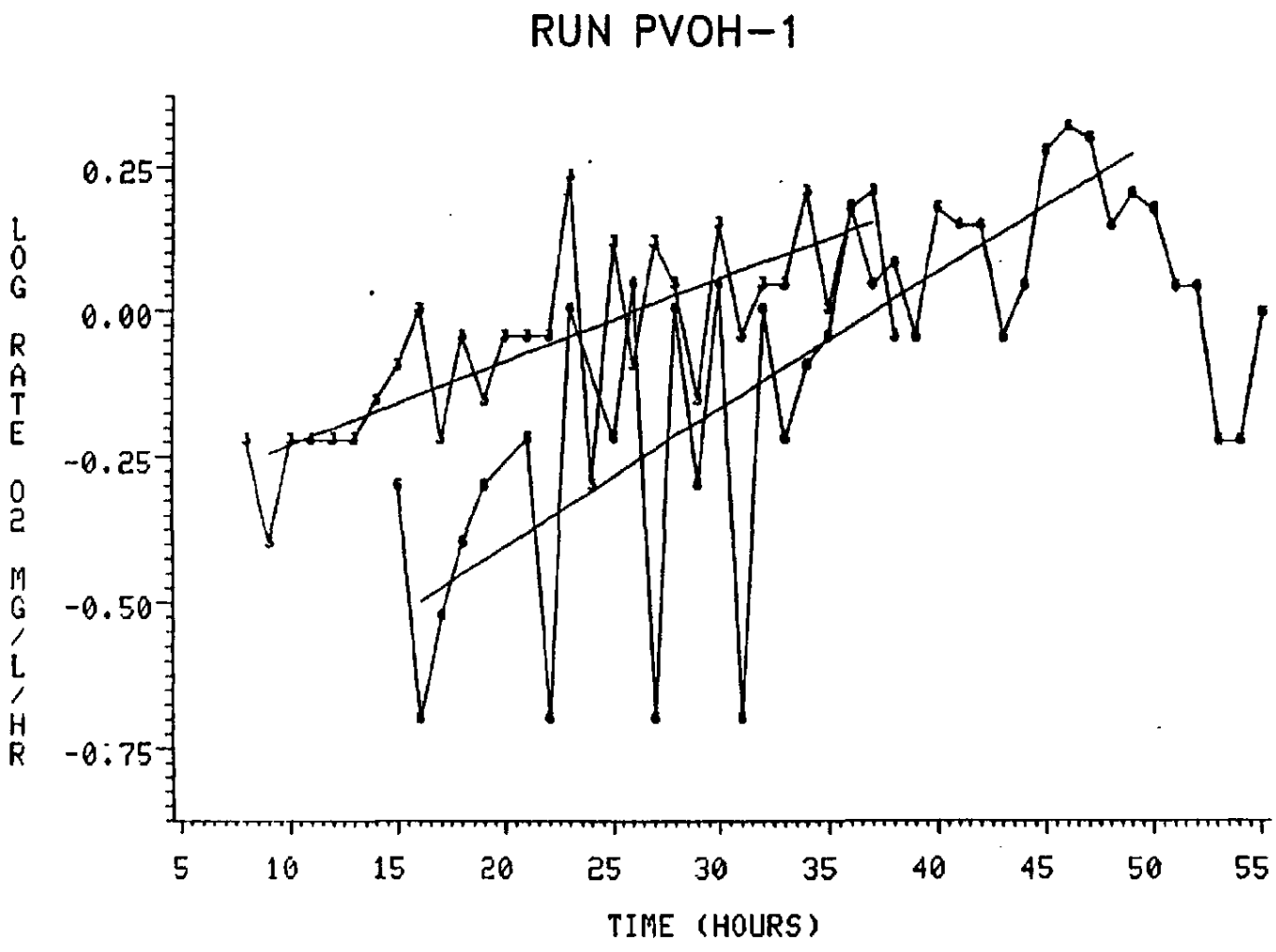


GROWTH RATE 3 =.01409 HR-1
GROWTH RATE 6 =.02342 HR-1

AP00018828

RESPIROMETER RUN PVOH-2

Cell #	1	2	3	4	5	6
SEED	-----ERG-SPRINGS MILLS BIOMASS FROM PVOH-1-----					
	/----washed cells----/			/---unwashed cells---/		
SUBSTRATE	Control	250 mg/l VINOL 205	250 mg/l VINOL 325	Control	250 mg/l VINOL 205	250 mg/l VINOL 325
INITIAL*						
pH	6.94	6.90	6.90	6.88	6.84	6.90
TOC (mg/l)	13.7	129	136	13.5	131	134
FINAL						
pH	7.06	6.64	6.83	6.91	6.57	6.79
TOC	12.4	18.7	19.9	13.4	18.5	20.1
TSS	249	447	409	236	379	373
VSS	211	373	318	204	306	295
%VSS	84.7	83.4	77.8	86.4	80.7	79.1
Δ(68 hrs)						
O2	9.2	239	265	14.8	256	278
TOC	1.3	110	116	.1	113	114
%TOC Red'n	9.5	85.5	85.4	.7	85.9	85.0
O2/TOC	7.07	2.17	2.28	148	2.27	2.44
ΔΔ						
O2		230	256		241	263
TOC		109	115		113	114
%TOC Red'n		94.5	93.9		95.7	94.4
O2/TOC		2.11	2.23		2.13	2.31

*This run started up with terminal materials from PVOH-1. Prior run made up with BOD nutrients, PO4 buffer with NH4Cl to give 28 ppm N per cell in 2,5 and twice that level in 3,6. Previously titrated to pH 7 with H3PO4, 20 mg/l ATU added to inhibit nitrification. Solids data not taken at end of run PVOH-1, hence no individual TSS/TOC nor solids O2 equivalence calculations for either run.

Polyvinyl alcohol solutions made up at 1 % by weight by suspension in cold water, warming to dissolution:

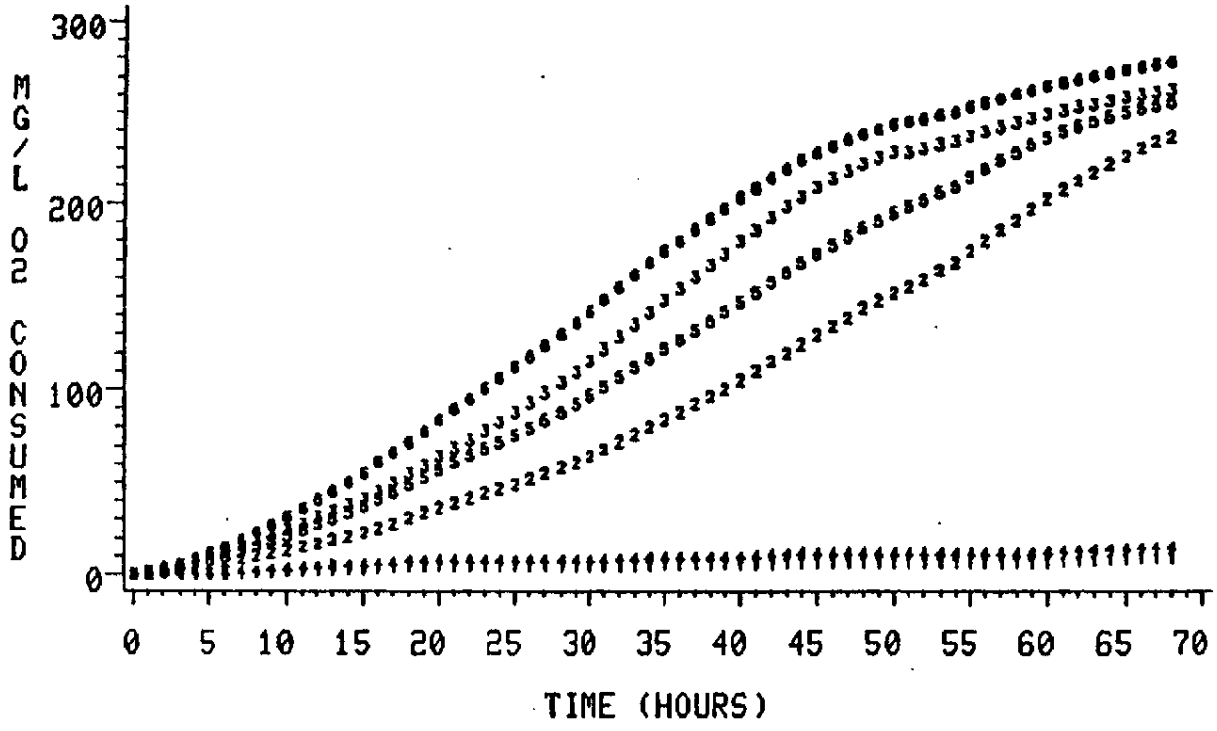
	VINOL 205	VINOL 325
hydrolysis :	partial - 88%	full - 98%
viscosity :	medium	low

J/j

032982-040282
NB 7018:55-61

AP00018829

ELECTROLYTIC RESPIROMETER RUN PVOH-2

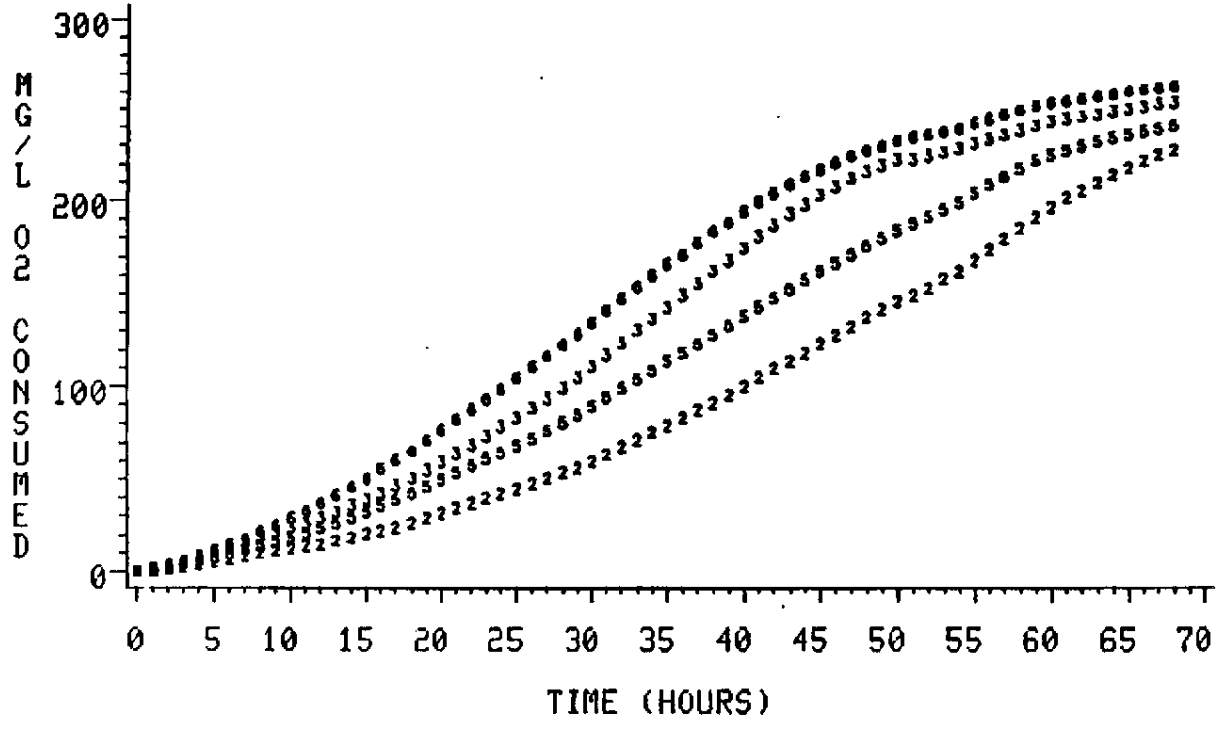


CELL 1 - WASHED ERG/SPRINGS MILLS BIOMASS
CELL 2 - 1 W 250 MG/L WT VINOL 205
CELL 3 - 1 W 250 MG/L WT VINOL 325
CELL 4 - UNWASHED ERG/SPRINGS MILLS BIOMASS
CELL 5 - 4 W 250 MG/L WT VINOL 205
CELL 6 - 4 W 250 MG/L WT VINOL 325

RUNDATE 032982-040182
REF BJK NB 7018:55-60

AP00018830

ELECTROLYTIC RESPIROMETER RUN PVOH-2



CELLS 2,3 - RESPIRATION OF WASHED ERG/SPRINGS MILLS
. BIOMASS CORRECTED FOR CONTROL CELL BIOMASS...
. ALLYLTHIOUREA ADDED FOR NITRIFICATION INHIBITION
CELLS 5,6 - RESPIRATION OF UNWASHED BIOMASS CORRECTED
. FOR CONTROL CELL BIOMASS ENDOGENOUS RATE RUNDATE 032982-040182
. AS ABOVE, NUTRIENTS ADDED FOR TEST ON TWO
. TYPES OF APCI POLYVINYL ALCOHOL @ 250 MG/L REF BJK NB 7018:55-60

AP00018831

RESPIROMETER RUN PVOH-2

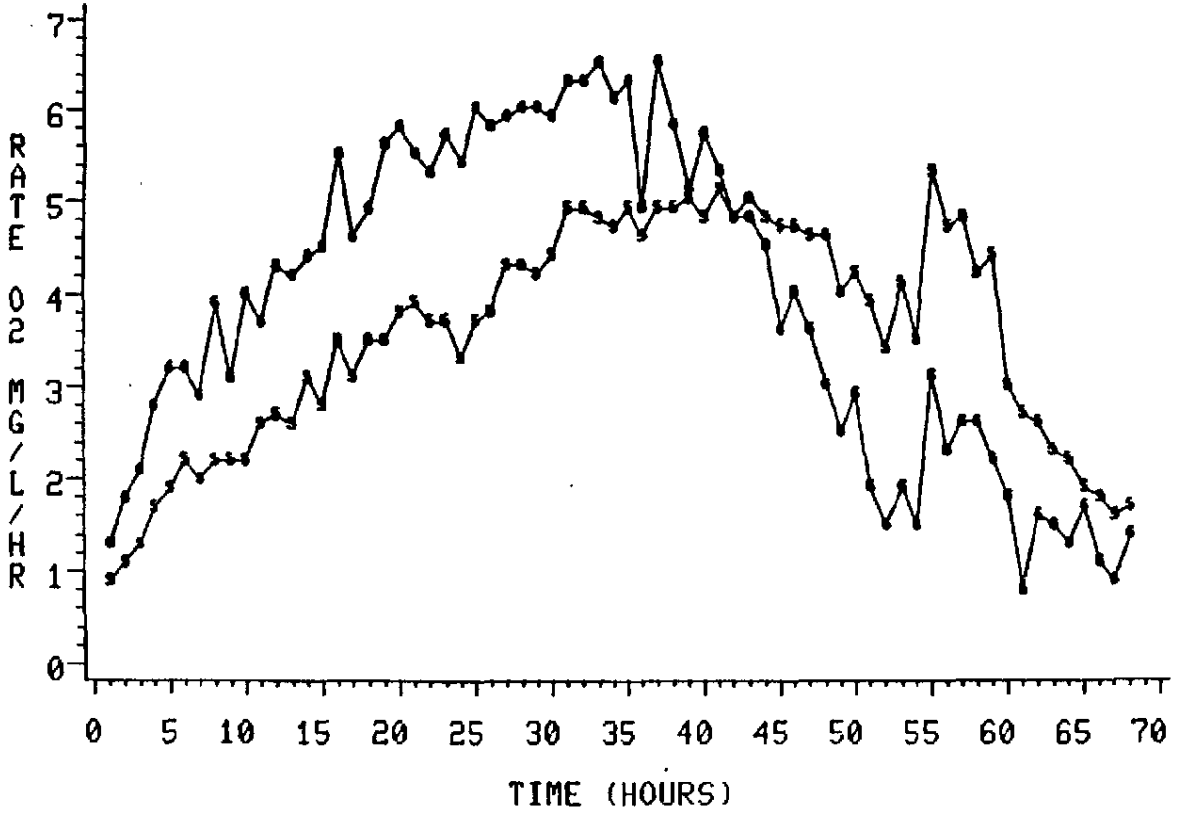
CELLS 2,3 - CORRECTED RATES FOR WASHED SLUDGE
. ON 250 MG/L VINOL 205, VINOL 325
.
.

RUNDATE 032982-040182
REF BJK NB 7018:55-60

AP00018832

AP00018833

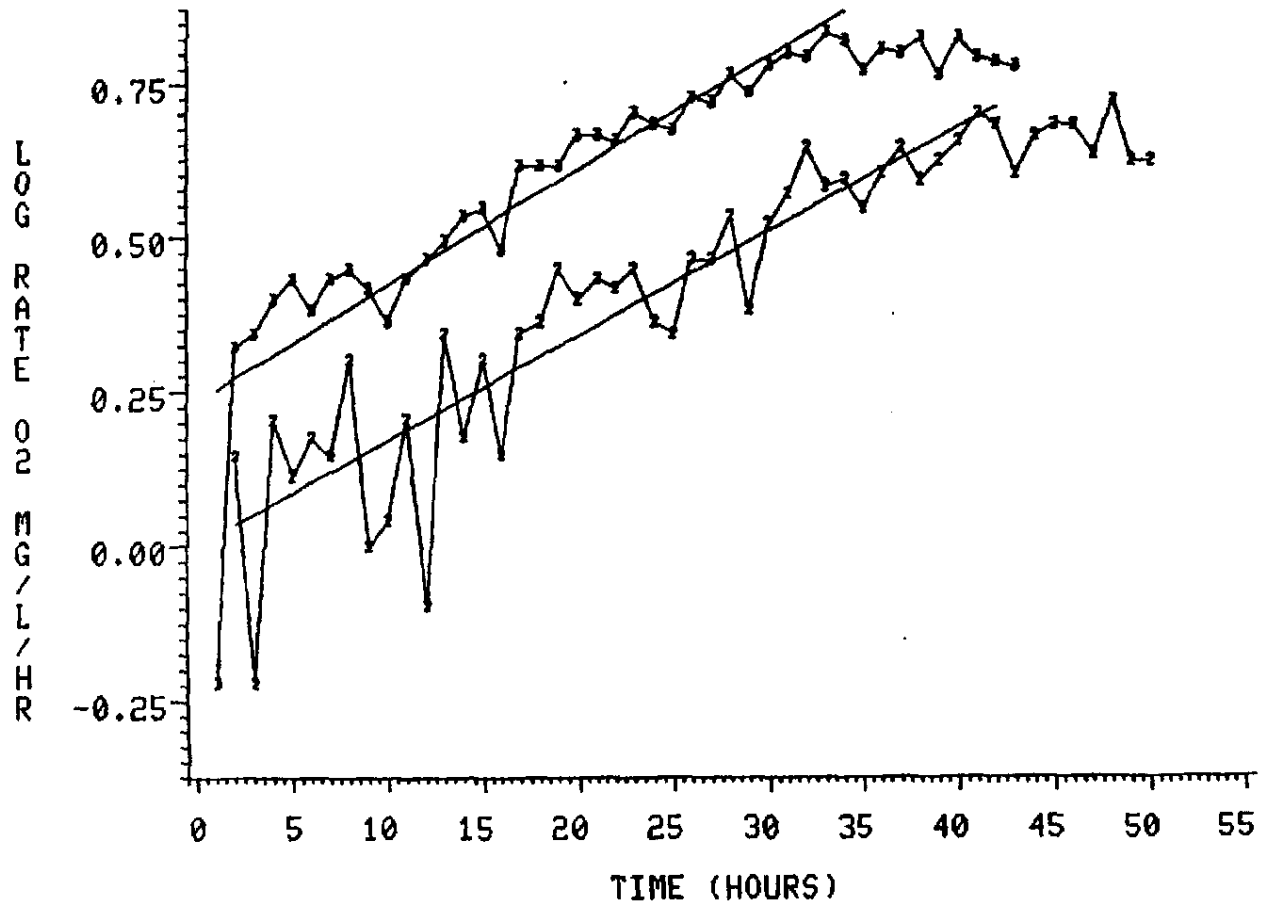
RESPIROMETER RUN PVOH-2



CELLS 5,6 - CORRECTED RATES FOR UNWASHED SLUDGE
ON 250 MG/L VINOL 205, VINOL 325

RUNDATE 032982-040182
REF BJK NB 7018:55-60

RUN PVOH-2



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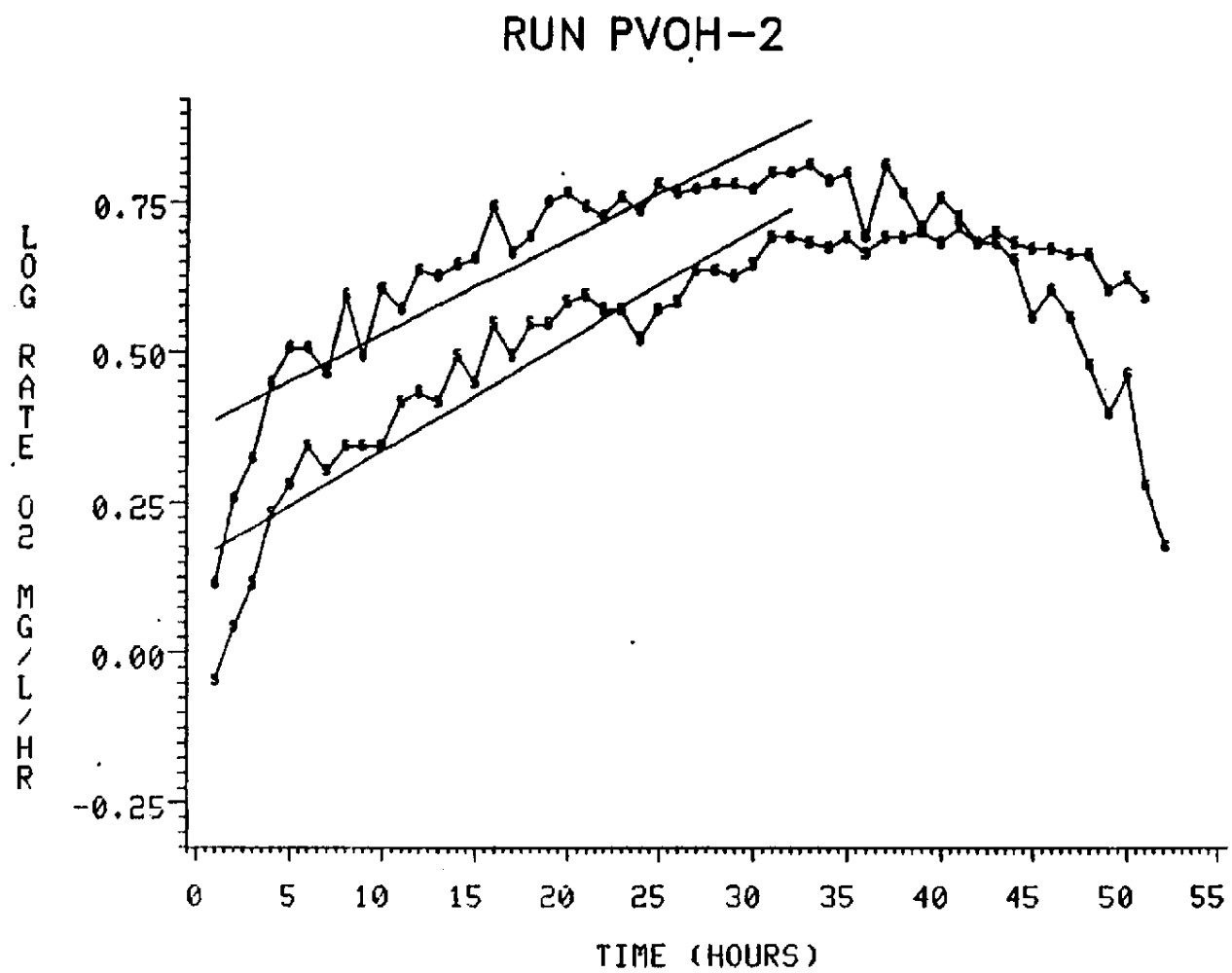
AP00018834



GROWTH RATE 5 =.01824 HR-1
GROWTH RATE 6 =.01568 HR-1

AP00018835

82-9.2

Risk Assessment for Vinyl Chloride in Perspective

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Air Pollution Control Association
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ATTACHMENT III

AP0018836

Introduction

The combination of circumstances which found the carcinogenic hazard of vinyl chloride (VC) being discovered at about the same time as the science of risk analysis was undergoing rapid development, and the great commercial interest and long history of use of the substance has resulted in a body of literature and pharmacological data greater than one can expect to have for most substances. It is therefore instructive to review the many risk assessments which have been prepared for VC against the available biological information to determine if we can evaluate the extrapolation methods used, and to discuss the current regulations for VC in light of this comparison.

Hazards of Vinyl Chloride

It is necessary to decide first which of the hazards presented by VC should be the basis for the risk estimation. The substance presents the acute hazards of frostbite from exposure to the liquid, of anesthesia at concentrations over 8,000 ppm and suffocation at higher concentrations (von Oettinger, 1955). It also forms explosive mixtures in air above 3.75 volume percent, and so the efforts to control the physical safety of operations generally preclude exposure to acutely toxic concentrations.

These control efforts were reinforced in the mid-1960's where it was discovered (Suciu, 1963) that workers who had been exposed to very high levels of VC developed "vinyl chloride disease," the primary manifestation of which was acroosteolysis (AOL), a degenerative disease of the bone tufts in the hands, and more rarely of the feet and lumbar region. Although crippling to some degree, this disease is not fatal, and is at least partially reversible if exposure is eliminated (Graniger, Walker and Ward, 1980).

Almost ten years later it was found that some of the workers having similar exposure also were developing angiosarcoma of the liver (ASL), a rapidly fatal disease. Oddly enough, there is only one possible case of a worker developing both AOL and ASL (Stafford, 1981) among the 80-plus cases of AOL and 90-plus cases of ASL now known worldwide, although both are diseases of the vascular system. Several large epidemiology studies were conducted on workers exposed to VC (Baxter and Fox, 1976; Chiazze, 1980; Duck, Carter and Coombu, 1975; Equitable Environmental Health, 1978; Fox and Collier, 1977; Frentzel-Beyme, Schnitz, and Theiss, 1978; Theriault and Allord, 1981), and ASL was the only fatal disease found consistently to be in excess in these

persons. Animal studies have shown an excess of tumors at other sites, but the lowest exposures at which these occur are considerably higher than that for ASL. For example, Maltoni (1979) reported the following data:

Site	Concentration For Significant Elevation
Forestomach papillomas:	30,000 ppm
Neuroblastomas:	10,000 ppm
Zymbal gland carcinomas:	10,000 ppm
Nephroblastomas:	250 ppm
Liver angiosarcoma male:	200 ppm, 50 mg/kg
female:	50 ppm, 16.7 mg/kg
Mammary adenocarcinoma:	5 ppm

The low concentration for onset of mammary tumors was of concern when a preliminary study of fabrication employees reported an excess of breast tumors (Chiazze, et al., 1979) but a follow-up case-controlled study (Chiazze, 1980) found no association between the cases and VC exposure. The largest study of VC-PVC workers in the United States reported slight excesses of brain and lung tumors (Equitable Environmental Health, 1978), but this was not seen in the other studies referenced above. The excess of brain tumors was small, and not dose- or exposure-related. The overall excess of lung tumors resulted from an excess in one plant only, and reexamination of those cases also showed no association with VC exposure (Waxweiler, 1978).

Vinyl chloride has been found to be active in several *in vitro* mutagenetic tests with bacteria and yeasts (Hopkins, 1979) and it appears to cause chromosome abnormalities in exposed workers, but these changes are reversible when exposure is reduced (Hansteene, 1978) and several studies of neighborhoods around PVC plants have failed to show a supportable association with birth defects (Edmonds, 1975, 1976). It is not a teratogen in rodents (Johns, 1977).

Therefore it appears reasonable to assume that if there is any significant chronic risk other than ASL, it is considerably smaller than that for ASL, and that an adequate risk assessment can be based on only the liver tumors.

NOTE TO EDITORS

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Review of Risk Assessments

1. Schneiderman, 1975

One of the first attempts to utilize animal data to estimate risks at very low exposures was that of Schneiderman, Mantel and Brown (1975). They used preliminary Maltoni results to compare the estimates obtained from three possible mathematical models. The 95% assurance level of a "safe" dose at a lifetime risk of 10^{-6} was estimated from several extrapolation models as follows:

Log Probit (slope = 1)	73 ppb
Logit (slope = 3.45)	119 ppb
Logit (slope 2.3, one-hit)	2.1 ppb

The authors discussed the recognized difficulties of extending these rat data to humans and of providing animal experiments that could answer satisfactorily the question of human risk at very low doses.

2. Kuzmack and McGaughy, 1975

The EPA was the first group to attempt a human risk assessment for vinyl chloride (Kuzmack and McGaughy, 1975). This pioneering effort attempted to use both animal and human data, and to show comparative results from both the linear and log-probit models. It concluded that there was an individual risk of 71×10^{-8} per ppm of lifetime exposure to VC by the linear extrapolation method, and that the log-probit results were one-tenth to one-hundredth of that.

This effort is subject to several serious criticisms. The exposure data used for human experience was that from a group with less than average exposure, while the ASL rate was chosen from only those plants which did report cases, and ignored the remainder of the population. Thus, their incidence rate of 7.5% compares to an actual figure of about 0.1%.

They used as their primary method a linear extrapolation of rat data, which often has been seen to overestimate the actual rates by at least two orders of magnitude, and they assumed the total cancer rate to be twice that found for ASL.

This same estimate was used by the EPA (1979) to estimate the concentration of VC in drinking water which would produce various levels of risk. These estimates are, of course, subject to the same criticisms.

Nisbet (1978) challenged the estimate of Kuzmack and McGaughy (1975) when it was used by Wilson in testimony before the OSHA hearing on its generic cancer policy. Nisbet stated that his calculations showed the risk to be 10-30 times greater, by the same calculation method. Wilson (1978) suggested several flaws

in the Nisbet procedure, including the fact that he chose for his extrapolation one point at 25 ppm from Maltoni experiment BT-15, and that this point is not in good agreement with the whole body of data. Further, he chose to use total cancer incidence in the rats, including those at zymbal glands, which have no counterpart in humans. Both Wilson and Kuzmack and McGaughy had used a factor of two times ASL to account for possible cancer at other sites. Wilson did acknowledge a mathematical error which made his results half the proper number.

Albert (1978) applied this same general procedure to other potentially carcinogenic air pollutants in the United States and calculated the expected annual cancer deaths as follows:

Arsenic	15.6
Benzene	77.8
Cadmium	26.2
Coke ovens	149.5
VC (after regulation)	1.0

3. Gehring, 1979

Gehring, et al., (1979) applied an experimentally derived biotransformation correction (Gehring, et al., 1978) to rat data and estimated the incidence in humans at two different exposures by means of four different extrapolation models. Their estimates at 500 and 200 ppm TWA bracket the observed experience for humans when derived from the probit and the unconstrained linear models. The linear-through-zero and one-hit models consistently overestimated the incidence. Although not considered by the authors, the linear and probit models match rather closely the total U.S. experience of occupational ASL at an assumed 1,000 ppm exposure. The linear model predicts no incidence below 99 ppm in humans. The probit model predicts a human risk of 1.5×10^{-8} at 1 ppm. Thus, a mechanism for adjusting for the difference in metabolism between animals and humans appears to be useful.

A limitation of the Gehring procedure is that it uses partial Maltoni data, and tests the results against the CMA epidemiology study. That study was not the "end of the experiment"; it stopped at the end of 1973, and several deaths have occurred since then. Neither did it cover the entire population, but only the employees of those plants which met certain critaria for data retention and length of operation. The Stafford (1981) data does cover the entire population and extends the history for seven years. The size of the population is not known, but a reasonable estimate, based on normal worker turnover rates and the number of plants not included in the CMA study, is certainly not less than 25,000. This would give a gross incidence of about 0.1%. Of these, the number actually exposed to substantial exposures would be about 25-30 per plant at any one time. Multiplication by 25 plants, and a factor of three for the turnover during this period, would give about 2,000 highly exposed persons, for an effective inci-

dence of just over 1%. Personal experience would indicate that, for the period prior to 1964, when all of the first exposures of the fatal 26 cases had occurred, the average exposures of this highly exposed group certainly was in excess of 1,000 ppm for the working day. Maltoni (1979) found a 1% incidence at about 1-10 ppm in rats. Calculation of the dose equivalent to a 1% incidence in rats gives 0 ppm by the linear method and 7.5 ppm from the log-probit equation for the combined Maltoni inhalation experiments. This crude and subjective estimate would then say that man is about 100 times as resistant as the rat to VC inhalation, a figure generally in agreement with other estimates (NCAB, 1979).

4. Food Safety Council 1978, 1980

The Food Safety Council has recommended (FSC, 1978) the use of the gamma multi-hit model because of its flexibility in handling dose response data of varying curvilinearity at low doses. It has calculated (FSC, 1980) the maximum likely and lower 97.5% limit doses for substances at various risk levels and with different models. For VC, at 10^{-6} risk, these results are as follows (based on early Maltoni data):

One-hit	2.0×10^{-2} ppm
Armitage-Doll	2.0×10^{-2} ppm
Weibull	2.1×10^{-9} ppm
Multi-hit	3.9×10^{-10} ppm

For this substance, the goodness of fit of the Weibull model (0.56) was superior to that of the multi-hit (0.32). Neither of the other two models gave acceptable fits. This was in part because of the concave shape of the curve, which included all of the high doses in the dose response data.

5. Dow, 1979

A Dow Heath Team performed a relative risk estimation for several compounds (Langer, et al., 1979) which considered probable exposure, the consequence of exposure, the physical state of the substance during processing, and the current exposure standards. This resulted in a value of 480 for VC in a "closed system but with employees in the vicinity." The same procedure assigned hazard rating values to some other substances as follows: benzene, 10; phosgene, 410; hydrogen sulfide, 5; arsine, 9,700; and bis-chloromethyl ether, 69,700. In a batch operation with occasional manual handling, the hazard rating for VC increased to 9,700 by this method.

6. Mehlr, 1980

Mehlr, et al., (1980) conducted a series of tests for the Consumer Product Safety Commission, a part of which consisted of exposing rats and mice to a series of short, high exposures, rather than

the usual extended low dosage. They included one-hour exposures to rats and mice at 50, 500, 5,000, and 50,000 ppm, 10 and 40 hour exposures at 500 ppm, and 49 and 100 one-hour exposures at 50 ppm. After lifetime observation they found no affects on rats, or their offspring, nor on mice exposed to less than 500 ppm. Those exposed to over 500 ppm developed pulmonary adenomas, but they also had suffered from pneumonitis.

They considered the published data on animal exposures and concluded that there was a lifetime dose below which no oncogenic response is seen. This was estimated to be 5,000 ppm-hrs for mice and greater than 50,000 ppm for rats, regardless of whether the dose was administered over a short or long period. This concept of equality of effectiveness for all modes of exposure does not have general acceptance and would not appear to be correct, based on our present understanding of carcinogenesis. Dose-rate effects are, of course, well known. However, the degree to which this can be extended to all types of effects is not known.

These authors also used the Crump-Guess model (Crump, Guess and Deal, 1977) to evaluate their data on mouse pulmonary cancer, and estimated that exposure to 5,000 ppm VC doubles the probability of cancer, while 50,000 ppm increased the risk nine-fold. In view of the fact that pneumonitis was present in all animals exposed above 500 ppm, it is questionable if this was a direct oncogenic response, or the result of an nongenetic event because of severe lung damage. Maltoni (1979) also reports an increase in lung tumors in mice, but not in rats or hamsters. Thus, the significance of this finding to risk in humans is questionable.

7. Anderson, 1980

Anderson, et al., (1980) extended the work of Gehring, et al., (1978 and 1979) to incorporate the amount of metabolic products from VC which actually was bound to the DNA of exposed rats, (Gehring and Blau, 1977) rather than the total amount metabolized. They assigned various values to the parameters in a Michaelis-Menten equation depicting the kinetics of the metabolic process, and compared the results from extrapolation to low doses by log-probit and multi-hit models. They found that the two extrapolation models responded quite differently to these variations at very low doses, and that it was not possible to select one model as the more appropriate from the high-dose data. Use of the values of Gehring for the primary parameters gave estimates of the dose equivalent to lifetime risks of 10^{-7} of less than 1 ppm for the probit model and less than 2 ppm for the multistage model, a correspondence which the authors pointed out was better than the precision of interspecies comparisons.

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8. EPA, 1980

The final version of the water quality criteria document for VC (EPA, 1980) used a different approach for risk estimation. The slope of the incidence of all tumors at the lowest doses of Maltoni experiment BT-1 was adjusted for the fraction of exposure, the equivalent feeding level to give the same blood concentration of VC as by inhalation (see Withey and Collins, 1976), and the ratio of the surface area of humans vs. rats, to produce an estimate that a lifetime risk of 10^{-5} would be caused by drinking 2 l/day of water containing 20 g/l. There is some confusion in the mathematics given in the report, and the assumptions on which the adjustments are made are far from having general acceptance, although generally following NAS recommendations. It appears that this procedure overstates the risk by several orders of magnitude.

9. NAS, 1980

The National Academy of Science (1977) calculated the upper 95% confidence limit for risk from drinking water containing vinyl chloride from the probabilistic multistage model and early Maltoni rat data. They report (NAS, 1980) a lifetime risk of 10^{-6} as being equivalent to $3.08 10^{-5}$ mg/kg/day. For a 70 kg person consuming 2 l/day, this would calculate to an acceptable level of 1 g/l. The difference between the EPA and NAS numbers comes from the different curve-fitting methods for the animal data.

10. Gaylor and Kodell (1980) applied linear "interpolation" to the same early Maltoni data used by the Food Safety Council (1978) to arrive at a predicted maximum risk of 10^{-6}. The upper 97.5% confidence limit of the animal data was taken as one point on the interpolative line, and zero incidence at zero exposure as the other. This produced a lower 97.5% confidence limit dosage of 7.1×10^{-4} ppm for a lifetime risk of 10^{-6} in rats. Their application of the Armitage-Doll multistage model gave 5.2×10^{-4} ppm as the dosage at 10^{-6} lifetime risk compared to 2×10^{-2} by the Food Safety Council. The difference is due to alternative assumptions on the value of the exponential dose term.

11. Crump and Guess (1980) reviewed some of the earlier risk estimates for vinyl chloride in drinking water, and recalculated the risks, using the one-hit and multistage models. They arrived at an upper 95% confidence limit of lifetime risk for drinking water containing 1 g/l of VC of 4×10^{-6}, based on early Maltoni inhalation data. Using the assumption that a 0.2% incidence of ASL in workers had resulted from a lifetime exposure of 70 g/kg, they obtained a maximum likelihood risk of 10^{-6} from 0.34 g/l by both the multistage and linear models, with 95% lower confidence limits of the same risk at 0.24 g/l. These two models reduce to a linear form when used at very low doses and with the assumption of no threshold value.

These authors cite EPA data on the occurrence of VC in public water supplies which by their methods yield a lifetime risk of 3.7×10^{-6}, or 12 deaths per year from this cause in the United States. None of these has been observed, despite the accumulation of 15 years' data on ASL deaths (Popper, 1978).

12. Scott (1981) ascribed the decreased incidence of tumors in rats at the higher doses to a cell killing process, and adopted the Weibull model to account for this. Application of the model to some early Maltoni data produced a curve which fit the data from 50-10,000 ppm. He did not attempt to extrapolate to doses beyond the experimental range.

13. Carlborg, 1981, also applied the Weibull model to 31 bioassay reports on a variety of animal carcinogens. He concluded that the one-hit model was not appropriate and that carcinogens could be divided into categories according to the shape of the curve, e.g., concave or convex. He found that the early Maltoni data on VC fell into the former category. Application of his parameter estimates to those data, assuming no spontaneous incidence of ASL, gives 2.5×10^{-6} ppm for a lifetime risk of 10^{-6} for rats. Later calculations including all of the published Maltoni data did not change the results significantly (personal communication).

He found the Weibull shape parameter to be approximately 0.5, which is assumed to be the number of stages for tumor initiation. This is consistent with the finding by Gehring (1977) of a saturable metabolic path which produces the proximate carcinogen. It also suggests that the number of "stages" is the number of fixiterate steps before the rate-limiting step. There may be other stages following, but they are not rate controlling. Actually, there appears to be at least two saturable mechanisms involved in the pharmacokinetics of VC, the metabolism to the ultimate carcinogen and the detoxification by sulfhydryl groups.

14. One further evaluation of human risk can be made from the experience of persons residing near VC-PVC plants. The EPA estimated (Kuzmack and McGaughy, 1975) that five million persons lived within five miles of these plants, and were exposed to an annual average concentration of 17 ppb. The present distribution of plants was generally well-established by 1959, thus we have 22 years of history, or about 110 million person-years. About five or six of these plants, with 1-2 million neighbors, go back another 20 years, but these data are not firm enough for inclusion.

The fact that no case of ASL has been confirmed as arising from these ambient exposures places the upper bound of risk at less than 2.7×10^{-7} per ppm-yr. It is believed that the exposure data were overestimated by EPA, and thus this result may be too low, but it is in the same general range as that arrived at by Gehring (1979) and Anderson (1980) after making corrections for pharmacokinetics.

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Extending this crude calculation, these five million persons are now supposed by EPA to be exposed to 0.2 ppb (probably a high figure), which would predict no more than 0.0003 deaths per year, or one per 3,700 years in that whole population due to VC exposure. But it also must be recognized that with approximately 20 cases per year of ASL in the general population, there can be expected from a purely statistical basis that there should be one case every two years or so among this group of 5 million plant neighbors.

The results of these estimates discussed above are compared in Table I, after conversion to a uniform 10^{-6} lifetime risk. Estimates 5, (Dow 1979) and 12 (Scott, 1981) were not in a form to permit this comparison. See OSHA, (1980), for references to a few other estimates that were not considered here.

It can be seen that the results fall into two major categories, those which project that the risk of 10^{-6} occurs at exposures of greater than 1 ppm, and those which find that risk in the ppb range. The estimates which yield the higher allowable exposures are based on human data (Nos. 3, 7 and 14) or use a log-probit extrapolation model (No. 2, second estimate), or predict a threshold (No. 6). The remainder generally are based on the linear, non-threshold model, and make no biological correction. The result is a difference of 3 or 4 orders of magnitude. The estimates which yield the higher allowable exposures are in better agreement with human experience than are those of the other group.

Additional Data

All of the extrapolations reported here have used for the original Maltoni data from his experiment BT-1. He has now reported (Maltoni, 1979) three other comparable inhalation experiments on the same strain of rats, and one on another strain, in addition to two ingestion studies. The results of these experiments are shown in Figure 1, on a log-probit scale. It can be seen that they all follow a similar pattern, but that there are large variations in slope between the various data groups. Table III contains the log-probit equations calculated from some of the individual experiments, and various groups of experiments. Excellent fits are obtained for a single experiment, as would be expected from the small number of data points, but adequate fits are obtained for the group as a whole. Inclusion of the historic control data on ASL (0.09% spontaneous incidence) did not affect the fit substantially, except for the very low dose data. Inclusion of the 0,0 (origin) as a data point did give significantly poorer fits. The combined experiments indicate that a lifetime risk of 10^{-6} for rats is obtained from a dose in the 1-2 ppb range.

Similar variation is seen with the other mathematical expressions, such as linear or exponential equations.

Regulatory Status

The current regulatory status of vinyl chloride is summarized in Table II. The first regulatory action on VC was taken in 1973 when the Bureau of Tax, Alcohol and Firearms prohibited the use of rigid PVC as liquor containers. This was based on it being present as an adulterant, and not on any consideration of risk. The Consumer Product Safety Commission (CPSC), the Food and Drug Administration, (FDA), and the EPA all acted to ban the use of VC as an aerosol propellant thus establishing a zero risk position. The FDA proposed (FDA, 1975) to withdraw the prior sanction status of rigid PVC as a food package component because of the concern for residual VC that might migrate. The FDA has taken no further action on this proposal, and now is considering a "constituent" policy which would permit a lifetime exposure at some acceptable risk level. This risk has been proposed recently to be 10^{-6} lifetime for the gluttonous consumer. As was discussed above, the EPA required a best available technology approach which reduces the average exposure to those within 5 miles of a plant to about 0.2 ppb, by EPA estimates. OSHA established a rule in 1974 which set 1 ppm for 8 hours as the maximum permissible exposure, and also set 0.5 ppm as an action level below which most features of the regulation did not apply. These were chosen as feasible levels, and not necessarily "safe" doses (OSHA, 1974; EPA, 1976).

The EPA has established an exposure to the general population only 0.1% of that allowed in the workplace. The CPSC has required zero exposure, and the FDA has considered that approach. Depending on which method of estimation the FDA may choose, its allowable exposure could be either greater or less than those currently set by EPA and OSHA. It has been estimated that the maximum amount of VC ingested by the average European, who uses much more plastic packaging than we, is less than 2_6 g/day, (CEFIC, 1976) which would be in the order of a 10^{-5} or 10^{-6} lifetime risk by even the most conservative models.

There have been various estimates made of the cost-effectiveness of the Federal regulation for vinyl chloride. Graham and Vaupel (1981) estimated that the OSHA rule cost $7.5 million per life saved, and $490 thousand per life-year saved over the option of leaving the exposure limit at 50 ppm. Luken and Miller (1981) state that the imputed value of a life from the OSHA standard is $4 million. Morrell (1982) uses an annual cost of $20 million and an annual benefit of 0.1 life saved to derive a cost/benefit of $200 million per life for the OSHA rule. The EPA has reported (EPA, 1979) that the cost of compliance with its VC standard was $296 million through July 7, 1981, and will be an additional $470 million during the next five years, all in 1977 dollars. If the EPA estimate of up to 20 deaths per year were correct, this would be a cost of $4.7 million per life. However, as discussed here, there is no evidence that any lives have been saved by this rule.

There are many difficulties in obtaining accurate estimates of this type, and serious problems in determining the proper value to be assigned to a life. Nevertheless, the doubtful nature of the claims

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for any significant benefit from these rules suggests that at best, these regulations are excessively costly to society. Therefore, we must attempt to improve both our data base and our methods for interpreting and applying the data.

Discussion

What can be learned from this exercise other than the already recognized fact that various extrapolation models can yield very different results? In this case, at least, there are several points which are worth considering.

1. Vinyl chloride is no exception to the rule that human data always must be incorporated whenever possible. The epidemic of occupationally induced ASL which was feared in 1974 has not materialized, probably due to the steps that were taken in the early 1960's to reduce exposure because of the discovery of ADL. No instances of ASL from exposure to VC in the general population have been substantiated. The overprediction of occupational cases was due to the underestimation of worker exposure and overreliance on raw animal data without proper pharmacokinetic adjustment. We are not now able to extrapolate reliably between similar species and certainly not from rodents to humans, without much additional data.

2. The regulations for vinyl chloride were not based primarily on scientific data, but on socioeconomic and political decisions. This is no surprise (Crandall and Lave, 1981), but is a fact which should be acknowledged openly, along with the understanding that this position will continue to penalize good science.

3. Mathematical extrapolation models are not adequate in themselves for predictions of risks much beyond the experimental range, no matter how good the fit is to the data in the observed range. The variability of relatively small experimental groups adds to the error range. Thus, bioassays intended for quantitative risk assessment applications should be at as low doses as possible, and as large as possible, and should be interpreted very cautiously.

4. The current state of the art is such that quantitative risk assessments may be useful for determining relative risks from similarly acting carcinogens, but are not suitable for across-the-board application to all mechanisms of carcinogenesis.

   This is not to say that we should abandon efforts at developing more effective risk assessment methods. We must, however, recognize the problems inherent in blind application of mathematical models without proper assessment of the available biochemical data, or an understanding of how applicable the experimental data are to humans.

We have available to us at least as much data regarding vinyl chloride as we have for any other substance, and we still have difficulty in deriving a suitable expression for risk from a purely mathematical or statistical basis. Only when human relevance is considered can we arrive at a prediction that approximates actual experience.

The regulators are faced with a tremendously difficult task when they are presented with a few pieces of animal data which suggest the need for concern and potential regulation. We must develop a suitable program to obtain and use as much relevant data as possible to assure that rational regulations are possible. The vinyl chloride experience can help us understand the kind of data which are needed.

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References

Albert, R. E., letter to R. S. Naveen, EPA, "Comparison of vinyl chloride carcinogenic risks with risk from other pollutants", Washington, DC, 16 June 1978.

Anderson, M. W., et al., Tox. Appl. Pharm. 55, 154 (1980).

Baxter, P. J., and A. J. Fox, Lancet, 1976 245.

Carlberg, F. W., Fd. Cosmet. Tox. 19 255 (1981).

CEFIC Committee for the Toxicity of Vinyl Chloride, "Vinyl Chloride Toxicity and the use of PVC for Packaging Foodstuffs," Brussels, Feb. 1976.

Chiazze, L., J. Occup. Med. 22 (10) 677 (1980).

Chiazze, L., Jr., W. E. Nichols, and O. Wong, J. Occup. Med., 19 623 (1977).

Crandall, R. W., and L. Lave, "The Scientific Basis of Health and Safety Regulations," Brookings Institution, Washington, 1981.

Crump, K. S., and H. A. Guess, "Drinking Water and Cancer", PB81-128167, December, 1980.

Crump, K. S., H. A. Guess, and K. L. Deal, Biometrics, 33 4370451 (1977).

Duck, B. W., J. T. Carter, and E. J. Coombes, Lancet 1975 ii, 1197.

Edmonds, L., "Birth Defects and Vinyl Chloride", Proc. Conference on Women and the Workplace, Washington, DC, 1976, also Teratology, 17 137 (1978).

Edmonds, L. D., M. Falk and J. E. Nissim, The Lancet 1975 1098.

Environmental Protection Agency, Standard for Vinyl Chloride, 41 Fed. Reg. 46,560 (1976).

Environmental Protection Agency "Vinyl Chloride, Ambient Water Quality Criteria", PB-292446, Washington, DC, 1979.

Environmental Protection Agency "Ambient Water Quality Criteria for Vinyl Chloride," EPA 440/5-80-078, October, 1980.

Environmental Protection Agency "The Cost of Clean Air and Clean Water", Annual Report to the Congress, December, 1979b. Senate Document No. 96-38. U.S. Government Printing Office, Washington, DC.

Equitable Environmental Health, Inc., "Epidemiological Study of Vinyl Chloride Workers, Final Report". Prepared for Manufacturing Chemists Assoc., Washington, DC, January, 1978.

Food and Drug Administration, Notice of proposed rulemaking, 40 Fed. Reg., 48,529 (1975).

Food Safety Council Final Report "Proposed System for Food Safety Assessment", Washington, DC, June, 1980.

Food Safety Council, Scientific Committee "Proposed System for Food Safety Assessment." Food and Cosmet. Tox. 16 Suppl. 2 December 1978.

Fox, A. J., and P. F. Collier, Br. J. Ind. Med. 34 1 (1977).

Frentzel-Beyme, R., T. Schmitz, and A. M. Thiess, Arb. Sozialmed. Prevent., 13 218 (1978).

Gaylor, D. W., and R. L. Kodell, R. L., J. Environ. Pathol. Tox. 4 305 (1980).

Gehring, P. J., and G. E. Blau, J. Environ. Pathol. Toxicol, 1 163 (1977).

Gehring, P. J., P. G. Watanabe, and C. N. Park, Tox. and Appl. Pharm. 49 15 (1979).

Gehring, P. J., et al., Tox. Appl. Pharmacol. 44 581 (1978).

Graham, J. D., and J. W. Vaupel, Risk Analysis 1 89 (1981).

Granger, R. G., A. E. Walker, and A. M. Ward "Vinyl Chloride Monomer-induced Disease: Clinical, Radiological and Immunological Aspects," Chapter 11 in "Induced Disease; Drug, Irradiation, Occupation", L. Prager, ed., Grune and Stratton, London, 1980.

Hanstaane, I.-L., et al., Mut. Res. 78 211 (1978).

Hehir, R. M., et al., "Toxicology, Carcinogenicity and Reproductive Effects of Single and Multiple Exposures to Vinyl Chloride in Rats and Mice", Pre-publication draft, Feb. 6, 1980, U.S. Consumer Product Safety Commission, Washington, DC.

Hopkins, J., Fd. Cosmet. Toxicol., 17 542 (1979).

John, J. A., et al., Tox. and Appl. Pharmacol. 39 497 (1977).

Kuzmack, A. M., and R. E. McGaughy, "Quantitative Risk Assessment for Community Exposure to Vinyl Chloride", U.S. EPA, Washington, DC, December 5, 1975.

Laegar, R. R., S. K. Norwood, G. E. Socha, and M. R. Moyle, Am. Ind. Hyg. Assn. J., (12) 1039 (1979).

AP0001843

ıken, R.H., and S. G. Miller, J. Air Pol. Control Assoc. 31 1254 1981).

ıltoni, C., G. Lefemine, A. Ciliberti, G. Cotti, and D. Carretti, /inyl) Chloride Carcinogenicity Bioassays, (B T Project) as an perimental Model for Risk Identification and Assessment in vironmental and Occupational Carcinogenesis" Presented at "Le Club Cancerogenese Chimique", Institute Curie, Paris, Nov. 10, 1979.

ıtional Academy of Science, "Drinking Water and Health", National :ademy Press, 1977.

ıtional Academy of Science, "Drinking Water and Health", Vol. 3, p. , National Academy Press, 1980.

ıtional Cancer Advisory Board, "The Relation of Bioassay Dose to the ıssessment of the Risk of Carcinogens for Humans under Conditions of w Exposure", Subcommittee on Environmental Carcinogenesis, Draft of 79, citing data from Meselson and Russell, 1979.

isbet, I.C.T., Post-hearing statement to OSHA docket 090, September , 1978.

:cupational Safety and Health Administration, Standard for Exposure Vinyl Chloride, 39 Fed. Reg. 35,890 (1974).

pper, M. et al., Am. J. Pathol. 92 349 (1978).

:hneiderman, M. A., N. Mantel, and C. C. Brown, Ann. NY Acad. Sci., 6 237 (1975).

:ott, B. R., Bull. Mathematical Biology, in press, 1981.

:afford, J., private communication (1981).

ıciu, J., J. Drejman, and M. Valaskai, Med. Intern. 15 967 (1963).

ıeriault, G., and P. Allard, J. Occup. Med., 23 (10) 671 (1981).

ın Oettingen, W. F., Public Health Service Publication No. 414, U.S. partment of Health, Education and Welfare, Washington, DC, 1955.

ıxweiler, R., et al., "An Epidemiological Investigation of an Excess ıng Cancer Risk in a Synthetic Chemicals Plant", Presented at the ineteenth International Congress for Occupational Health, Dubrovnik, go., Sept., 1978.

ılson, R. "Response to comments of I. C. Nisbet," Post-hearing record HA Docket 090, 1978.

ithey, J. R., and B. T. Collins, J. Tox. Envir. Health, 2 311 (1976).

FIGURE 1
GRAPHICAL REPRESENTATION OF TABLE III
LOG-PROBIT PLOT

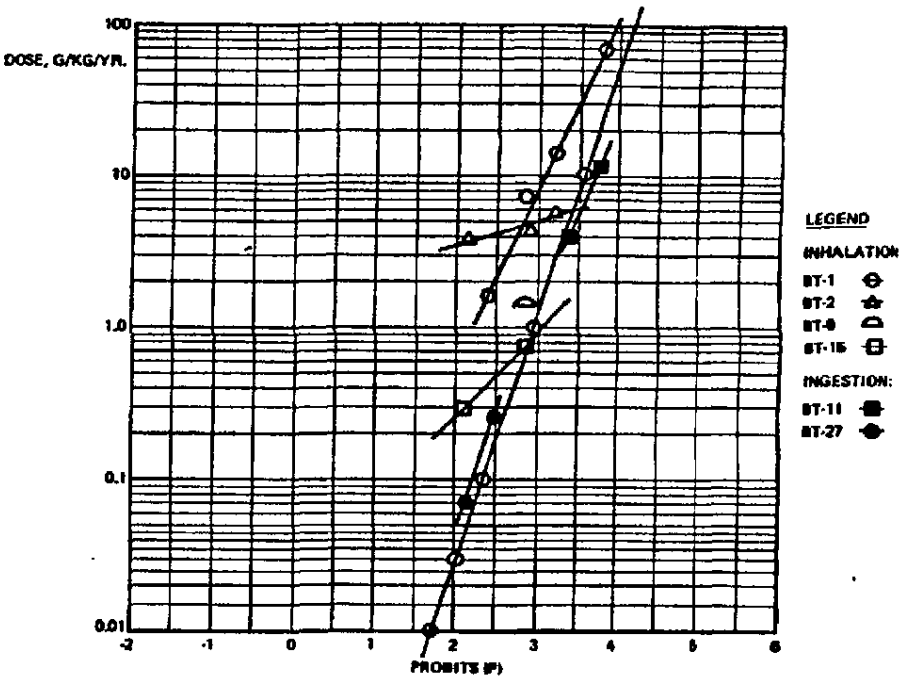

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TABLE I
SUMMARY OF
QUANTITATIVE RISK ASSESSMENTS FOR VC

ESTIMATE NO.	AUTHOR	BASE SPECIES	EXPOSURE FOR 10^{-6} LIFETIME RISK	COMMENTS
1	SCHNEIDERMAN, 1975	RAT	73 ppb 119 ppb 2 ppb	LOG-PROBIT LOGIT SLOPE = 3.45 LOGIT SLOPE 2.3, 1-HIT
2	KUSMACK & McGAUGHY, 1976	RAT, HUMAN	14 ppb 140-1400 ppb	LINEAR THROUGH ZERO LOG-PROBIT
3	GEHRING, 1975	RAT, HUMAN	>1 ppm	BIOTRANSFORMAL DATA AND LINEAR OR LOG-PROBIT
4	FOOD SAFETY COUNCIL, 1980	RAT	2×10^{-6} ppb	WEIBULL
6	HEHIR, 1980	RAT, MOUSE	THRESHOLDS SEEN IN BOTH SPECIES	
7	ANDERSON, 1980	RAT, HUMAN	>1 ppm	DNA BINDING
8	EPA, 1980	RAT	4 μ G/DAY	FOOD OR WATER
9	NAS, 1980	RAT	3×10^{-5} MG/KG/DAY	WATER
10	GAYLOR & KODELL, 1980	RAT	0.7 ppb 0.5 ppb	UPPER 97.5% CONFIDENCE LIMIT OF LINEAR MODEL ARMITAGE-DOLL MODEL
11	CRUMP & GUESS, 1980	HUMAN RAT	0.7 μ G/DAY 0.5 μ G/DAY	APPLYING WORKER DATA TO WATER, UPPER 95% CONFIDENCE LIMITS
13	CARLBORG, 1981	RAT	2.5×10^{-5} ppb	WIEBULL
14	THIS PAPER	HUMAN	>1 ppm	NEGATIVE EPIDEMIOLOGY

TABLE II
REGULATORY STATUS OF VINYL CHLORIDE

AGENCY	CONTROLLED LEVEL	PHILOSOPHY
BATF	BANNED AS LIQUOR BOTTLE	ADULTERANT
CPSC	BANNED IN CONSUMER PRODUCTS	ZERO RISK
FDA	USE IN RIGID FOOD PACKAGING QUESTIONED	CONSIDERING ACCEPTABLE RISK
EPA	APPROXIMATELY 0.2 ppb	BEST AVAILABLE TECHNOLOGY
OSHA	1 ppm 8-HR TWO MAXIMUM 0.5 ppm ACTION LEVEL	LOWEST FEASIBLE LEVEL

AP00018845

TABLE III
EQUATIONS FOR CURVES FITTED TO VARIOUS SINGLE AND COMBINED MALTONI EXPERIMENTS

EXPERIMENT	LINEAR y=ax + b			LOG PROBIT P=a IN DOSE + b			CONCENTRATION AT 10^{-5} RISK, (LOG-PROBIT), ppm
	a	b	r	a	b	r	
BT-1	0.26	3.36	0.97	0.35	2.76	0.99	0.03
PLUS CONTROLS	0.27	2.47	0.97				
BT-2	3.05	-8.59	1.0	1.60	0.88	1.0	23
PLUS CONTROLS	1.52	-1.13	0.88				
BT-15	6.5	-1.06	1.0	0.69	3.46	1.0	0.34
PLUS CONTROLS	5.28	-0.30	0.95				
ALL INHALATION STUDIES (4)	0.26	3.07	0.91	0.27	2.98	0.82	0.002
PLUS CONTROLS	0.27	2.80	0.91				
ALL INGESTION STUDIES (2)	1.75	0.15	0.95	0.30	3.22	0.88	0.002
PLUS CONTROLS	1.74	0.20	0.95				
ALL STUDIES (8)	0.29	3.60	0.73	0.27	3.05	0.82	0.001
PLUS CONTROLS	0.29	3.41	0.72				
ALL STUDIES; LOW DOSES ONLY				0.51	2.53	0.76	0.42
PLUS CONTROLS	1.03	0.97	0.79	0.17	2.71	0.49	0.0002

82-9-2

Update on Regulatory Status

EPA

Vinyl chloride standard revisions under discussion with SPI.
OMB approved change to semiannual reports.
Additional suits filed and Sec. 114 letters sent on emergency emissions.
PMN exemption policy excludes VC, etc.
Study of emissions, including VC underway in Harris Co., Texas.
Superfund reporting limits in revision, VC may stay at 1 lb.
Revised Test Methods 106 and 107 published 7 and 8 September.

OSHA

Comment period is closed on proposal to reopen the cancer policy - action next year?
Comment period closed on revision of medical record retention rule.
Labeling rule not expected until mid-83.
Noise standard generally in effect.
Respirator rule comment period over.
VC Training Film now available from National Audiovisual Center.
Voluntary programs now in pilot phase.

FDA

Promised action on 1975 PVC proposal this October.
Constituent policy comment period closed.
No action on plasticizers - more tests.

Others

Unpublished report suggest tumors from VAc exposure.
Peroxides cause skin tumors in an 8(e) report.
TCE bioassay being reviewed this month.

States

Many have own labeling, wastes, etc. rules.