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Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Draft Agenda

1. Opening Session
2. Election of Chairman, Vice-Chairman and appointment of Rapporteurs
3. Adoption of Agenda
4. Toxicity of coagulant aids
 - 4.1 Introduction of the background paper by the authors
 - 4.2 Statements by the participants
 - 4.3 General discussion
 - 4.4 Recommendations and guidelines
 - 4.5 Final conclusions
5. Toxicity of uPVC pipes
 - 5.1 Introduction of the background paper by the authors
 - 5.2 Statements by the participants
 - 5.3 General discussion
 - 5.4 Recommendations and guidelines
 - 5.5 Final conclusions
6. Discussion of the final report
7. Closure of the meeting

International Reference Centre
for Community Water Supply



Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Annotated Draft Agenda

Thursday, 8 February

- | | | |
|---------------|-----|---|
| 9.00 - 9.30 | 1. | Opening Session |
| | 1.1 | Opening of the meeting by the Director IRC/CWS |
| | 1.2 | Statement by WHO Representative |
| | 1.3 | Short review of work IRC/CWS by Manager IRC/CWS |
| | 2. | Election of Chairman, Vice-Chairman and
appointment of Rapporteurs |
| | 3. | Adoption of Agenda |
| | 4. | Toxicity of coagulant aids |
| 9.30 - 9.40 | 4.1 | Introduction of the background paper by the
authors |
| 9.40 - 10.30 | 4.2 | Statements by the participants |
| 10.30 - 10.45 | | Coffee Break |
| 10.45 - 12.30 | 4.3 | General discussion |
| 12.30 - 13.30 | | Lunch Break |
| 13.30 - 15.15 | | General discussion |
| 15.15 - 15.30 | | Tea Break |
| 15.30 - 17.00 | 4.4 | Recommendations and guidelines |
| | 4.5 | Final conclusions |

Friday, 9 February

- | | | |
|--------------|-----|--|
| | 5. | Toxicity of uPVC pipes |
| 9.00 - 9.15 | 5.1 | Introduction of the background paper by the
authors |
| 9.15 - 10.45 | 5.2 | Statements by the participants |

10.45 - 11.00		Coffee Break
11.00 - 12.30	5.3	General discussion
12.30 - 13.30		Lunch Break
13.30 - 15.15		General discussion
15.15 - 15.30		Tea Break
15.30 - 17.00	5.4	Recommendations and guidelines
	5.5	Final conclusions

● Saturday, 10 February

9.00 - Continuation of discussions on toxicity of coagulant aids or toxicity of uPVC pipes, depending on progress during former days.

Saturday, 10 February / Sunday, 11 February

Preparation of final report by Rapporteurs, authors of the background papers and the secretariate (Representatives of WHO and IRC). The report will be made available to the participants on the evening of Sunday.

● Monday, 12 February

9.00 - 10.30	6.	Discussion of the final report
10.30 - 10.45		Coffee Break
10.45 - 12.00		Discussion of the final report
12.00 - 13.00		Tour of Institute
13.00 - 14.00		Lunch Break
14.00 -		Discussion of the final report
	7.	Closure of the meeting



Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

General Objective of the Meeting

To reconcile the difference in the studies and in the procedures adopted in different countries, through a consultation of experts and to produce guides on the health hazards of using uPVC pipes and synthetic coagulant aids - identifying the nature of the hazards, toxic components, testing procedures, users' specifications and recommended procedures for the formulation and administration of standards by governments at national level, and delineation of areas of research and co-ordination at international level.



Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

List of Participants

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- WHO Head Quarters Geneva

Mr. D.V. Subrahmanyam - Community Water Supply and Sanitation Unit
Division of Environmental Health
World Health Organization.

- WHO International Reference Centre for Community Water Supply

Prof. W.F.J.M. Krul, Advisor I.R.C.
Member of Panel of Experts WHO

Ir. P. Santema, Director I.R.C.

Drs. J.M.G. van Damme, Manager I.R.C.

Ir. A. Kepinski

Ir. T.K. Tjiook

Mrs. M.L. Broersma

- Testing and Research Institute of the Netherlands Waterunder-
takings KIWA Ltd.

Dr. C.L.M. Poels, Toxicologist

Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Background document 4.2/1
Restricted

Statement on the toxicity of coagulant aids
(draft agenda item 4.2)

by

Dr. V. Benes, Chief
Division of Toxicology and
Reference Laboratory
Institute of Hygiene and
Epidemiology
Prague, Czechoslovakia

The Use of Polyelectrolytes in Water Treatment

Statement by Dr. V. Benes

From the toxicological point of view it is necessary to pay attention, in the first place, to water-soluble monomers contained in generally used polyelectrolytes that migrate into drinking water. Residual quantity of monomers depends on their concentration in trade products and dose used for water treatment. Specification of trade preparations, especially so far as the content of toxic monomers is concerned, is therefore necessary. It may be presumed that toxicological tests, for example with polyacrylamide, cover also toxicological evaluation of the monomer up to the content of 0.08 % in the polyacrylamide tested and comparison of the possible content of the residual monomer with toxicological results offers a relatively high "safety factor".

Nevertheless, it may be considered desirable to evaluate the hazard of monomer microquantities on the international level by means of the procedure of establishing the ADI (acceptable daily intake). Also residual monomers of the rest of polyelectrolytes used should be submitted to the procedure in question. Evaluation of the hazard of microquantities of residual monomers on the international level would be useful for establishing international as well as national standards, determining application conditions, general and specific recommendations and similar.

In evaluating residual microquantities of chemical substances in drinking water resulting from water treatment the WHO should proceed in the same way as in the case of toxicological evaluation of the hazard for example of chemical substances in foods (additives, pesticide residues and other contaminants).

It is highly desirable and necessary for the WHO to establish

and convene, from time to time, a group of experts that should make use of the experience and system of work of the existing WHO expert committees with specific regard and pertaining modifications for drinking water (for example percutaneous exposure). Such a group of experts should be engaged not only in polyelectrolytes but also all the rest of chemical contaminants or additives in drinking water so far as they are not evaluated from the toxicological point of view by other expert groups (for example Joint FAO/WHO Expert Committees on Food Additives; Joint FAO/WHO Meetings on Pesticide Residues).

This way of approach may be considered to be by far more effective than establishment of national toxicological committees at first and their subsequent co-ordination by the WHO.

WHO INTERNATIONAL REFERENCE CENTRE FOR COMMUNITY WATER SUPPLY

Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Background document 4.2/2
Restricted

Statement on the toxicity of coagulant aids
(draft agenda item 4.2)

by

The Water Research Association
Marlow, Buckinghamshire
England

Expert meeting on the toxicity of uPVC pipes and coagulant aids.

The Hague, 8 - 12th February, 1973

Summary statement of WRA

The use of polyelectrolytes in water treatment

An increasing number of water authorities in the United Kingdom use polyelectrolytes either as coagulant aids (floc conditioners) in water purification or as flocculants in the thickening and filtration of waterworks sludge. Although the older coagulant aids such as activated silica and sodium alginate are still used at several waterworks these have been supplanted in many cases by starch derivatives and polyacrylamide based materials. Polyelectrolytes have not been employed continuously on a large scale to replace conventional hydrolysing coagulants as up to now no technical or economic advantages of doing so have been established.

The Committee on New Chemicals for Water Treatment was formed in 1966 'to assess the possible hazards to health of new chemicals proposed for the treatment of water for public supply and to advise on the conditions ensuring their safety in use'. The seventh statement of the Committee is attached and this lists in Appendix 1, 45 polyelectrolytes considered to be unobjectionable on health grounds. In the United Kingdom the responsibility for supplying a 'wholesome' water to the consumer rests with the individual water authorities and the role of the Committee is therefore purely advisory. In practice however water authorities do not use polyelectrolytes that have not been approved by the Committee.

The following principles which have been adopted by the Committee on New Chemicals for Water Treatment are considered to be of the utmost importance.

1. Applications for consideration by the Committee of new products are only accepted from manufacturers. This ensures that full information on the product is available and that appropriate guarantees can be given. The only exception to this rule is when a product that has already been approved by the Committee is to be resold under a different trade name. In this case the company reselling the product has to guarantee that the new named product will never be other than the product already approved.
2. The manufacturer has to provide some evidence of the effectiveness of his product if this is an entirely new type of material. The object of this is to prevent the time of the Committee being taken up by considering useless products.
3. It is entirely the responsibility of the manufacturer to provide the Committee with appropriate toxicological information. The role of the Committee is to consider this information, if necessary to request more information, then to approve or reject the product.
4. In considering possible hazards to health arising from the use of any particular chemical no allowance is made for the removal of that chemical in the treatment process as this can be affected by plant design and operator efficiency. In any case it has been shown that acrylamide monomer is not removed significantly in flocculation and filtration.

In the near future a scheme will be instituted in the UK in which water authorities using polyacrylamide based products will periodically send samples to the Department of the Environment to be checked for monomer content.

Concern has been expressed recently at the widespread use of polyacrylamides of unregulated monomer content outside the Water Industry for example in the production of sand, gravel, coal and paper. Work at the WRA (see Table 1) has shown that effluents from these industries may contain acrylamide at levels greatly in excess of those allowed in water for public supply

TABLE 1

Effluent	Acrylamide concentration $\mu\text{g/litre}$
Colliery A Tailings Lagoon	42
Colliery B Tailings Lagoon	39
Colliery C Coal washing effluent lagoon	1.8
Colliery/coking plant effluent	0.74
Paper mill A treated effluent	0.47
Paper mill B treated effluent	1.2
Clay pit effluent	16
Sewage effluent (containing waste from chemical manufacturer using acrylamide)	1100

In considering the figures in Table 1 it should be borne in mind that on the basis of the specification of the Committee on New Chemicals for Water Treatment, the average level of acrylamide in potable water should not exceed $0.25 \mu\text{g/litre}$.

COMMITTEE ON NEW CHEMICALS FOR WATER TREATMENT

SEVENTH STATEMENT

1. In September 1966 the then Minister of Housing and Local Government set up a Committee to assess the possible hazards to health of new chemicals proposed for the treatment of water for public supply, and to advise on the conditions ensuring their safety in use. The terms of reference of the Committee have been extended to include new chemicals for use in swimming pools.
2. The appendices to this statement show a complete list of those products that the Committee consider, subject to certain conditions, to be unobjectionable on health grounds for the treatment of water for the purposes indicated. The Committee have not commented on the technical merits of any of these products and their inclusion in this list should not be taken to imply any recommendation as to their effectiveness in use.
3. The Committee will be interested to hear from any undertaking on their experience with the use of any products listed in the appendices. The information should be sent to The Secretary, Committee on New Chemicals for Water Treatment, Department of the Environment, Room C5/05, 2 Marsham Street, London SW1P 3EB.
4. This statement supercedes all previous statements.
5. Since the sixth statement was published the following changes have been made to the list.

ADDITIONS

APPENDIX I

ARIPOL F1, DECAPOL C330P, C300P and N100P, BTI C100(PWG) and CL10(PWG), NALFLOC N607
MAGNAFLOC LT20, FLOCCOTAN 'A', DECAPOL C100P, POLYMERS 233, 243 and 253

APPENDIX III

VAPORIN, FI-CLOR 60S and 91.

DEPARTMENT OF THE ENVIRONMENT

SEPTEMBER 1972

COMPLETE LIST OF PRODUCTS FOUND BY THE COMMITTEE TO BE UNOBJECTIONABLE ON HEALTH GROUNDS FOR THE TREATMENT OF WATER FOR PUBLIC SUPPLY.

A. PRODUCTS BASED ON POLYACRYLAMIDE, POLYACRYLIC ACID OR ACRYLAMIDE/ACRYLATE COPOLYMERS.

For these products the following conditions apply;

- i. No batch must contain more than 0.05% monomer acrylamide.
- ii. The dose used must average no more than 0.5mg/l and never exceed 1 mg/l.
- iii. An upper limit for the content of monomer acrylamide must be stated by the supplier for every batch.
- iv. The method of analysis for acrylamide is that described by the Water Research Association Technical Inquiry Report No 171, except where otherwise stated.

BTI A100(PWG)
BTI A110(PWG)
BTI A130(PWG)
BTI A150(PWG)
BTI C100(PWG)
BTI C110(PWG)
BTI M100(PWG)

B.T.I. Chemicals Ltd,
Bowling Park Drive,
Bradford,
Yorkshire,
BD4 7ES

DECAPOL A30P
DECAPOL A33P
DECAPOL A39P
DECAPOL A45P
DECAPOL C30OP
DECAPOL C33OP
DECAPOL M10OP

Fospur Ltd,
Alfreton Industrial Estate,
Nottingham Road
Summercotes,
Derbyshire

FLOCBEL 160FG

Float-Ore Ltd,
Apex Works
Willowbanks,
Uxbridge,
Middx.

MAGNAFLOC LT20
MAGNAFLOC LT22
MAGNAFLOC LT24
MAGNAFLOC LT25
MAGNAFLOC LT26

Allied Colloids Manufacturing Co. Ltd.,
Low Moor,
Bradford,
Yorkshire,
BD12 0JZ

NALFLOC A373
NALFLOC A375
NALFLOC A378
NALFLOC N671

Nalfloc Ltd,
PO Box 11,
Northwich,
Cheshire,
CW8 4DX

POLYFLOK POWDER 365P
POLYFLOK POWDER 430P

Yorkshire Chemicals Ltd
27, Kirkstall Road,
Leeds 3,
Yorkshire

SUPERFLOC 992

Cyanamid of Great Britain Ltd,
Bush House,
Aldwych,
London WC2

ARIPOL F1

Berk Ltd
Stratford
London
E15 3NX

PURIFLOC N17
PURIFLOC A22

Dow Chemical Co (UK) Ltd,
105, Wigmore Street,
London W1

For both PURIFLOC N17 and A22 the method of analysis for the determination of acrylamide to be used is that published in ANALYTICAL CHEMISTRY, VOL 37, Page 1546, November 1965.

POLYMER 233
POLYMER 243
POLYMER 253

Chemviron S.A.
PO Box 17
Ixelles 1
B1050 Brussels
Belgium

B. PRODUCTS BASED ON STARCH

For these products the following conditions apply;

- i. The dose used must not exceed 2 mg/l.

PERFECTAMYL A5114/2
PERFECTAMYL A5114/2 (without boron)

Messrs Avebe GA,
Veendam,
Holland.

JM 67

J.M.(Chemicals) Ltd,
5 Wellfield,
Manor Farm,
Hazlemere,
Bucks.

- ii. The dose used must not exceed 3 mg/l.

WISPROFLOC P

W.A.Scholten's Chemische Fabrieken NV
Foxhol
Postbus 1
Holland.

- iii. The dose used must not exceed 5 mg/l.

WISPROFLOC 20

W.A.Scholten's Chemische Fabrieken NV
Foxhol,
Postbus 1
Holland.

C. PRODUCTS BASED ON SODIUM ALGINATE.

For this product the following condition applies;

- i. The dose used should not normally exceed 1 mg/l.

WELGUM S

Alginate Industries Ltd,
22 Henrietta Street
London WC2

D. PRODUCTS BASED ON TANNIN.

For these products the following condition applies;

- i. The dose used should not normally exceed 10 mg/l (calculated on the dry product)*

FLOCCOTAN A
FLOCCOTAN M

Dearborn Chemicals Ltd
Widnes,
Lancashire.

E. PRODUCTS BASED ON QUARTERNARY AMMONIUM POLYELECTROLYTE

For this product the following condition applies;

- i. The dose used must not exceed 7 mg/l

CATFLOC

Calgon Corporation
Water Management Division
Calgon Centre,
Box 1346,
Pittsburgh PA 15230
USA

F. PRODUCTS BASED ON POLYAMIDE.

For these products the following condition applies;

- i. The dose used must not exceed 10 mg/l

SUPERFLOC 521

Cyanamid of Great Britain Ltd
Bush House
Aldwych
London WC2

DECAPOL CLOOP

Fospur Ltd
Alfreton Industrial Estate
Nottingham Road
Somercotes
Derbyshire

* FLOCCOTAN M IS AVAILABLE IN EITHER SOLID OR LIQUID FORM.

G. PRODUCTS BASED ON POLYAMINE

For this product the following condition applies;

- i. The dose used must not exceed 7.0 mg/l

NALFLOC N607

Nalfloc Ltd,
P.O. Box 11,
Northwich
Cheshire.
CW8 4DX

45

APPENDIX II

COMPLETE LIST OF PRODUCTS FOUND BY THE COMMITTEE TO BE UNOBJECTIONABLE
ON HEALTH GROUNDS FOR USE AS ADDITIVES IN SEA WATER DISTILLATION PLANTS
USED TO PROVIDE POTABLE WATER

PRODUCTS BASED ON POLYACRYLAMIDE, POLYACRYLIC ACID OR
ACRYLAMIDE/ACRYLATE COPOLYMERS

For this product the following conditions apply;

- i. No batch may contain more than 0.5% free acrylic monomer.
- ii. The dose used must not exceed 10 mg/l.

VAPTREAT H

Houseman and Thompson Ltd
The Priory
Burnham
Bucks

APPENDIX III

COMPLETE LIST OF PRODUCTS FOUND BY THE COMMITTEE TO BE UNOBJECTIONABLE ON
HEALTH GROUNDS FOR USE IN SWIMMING POOLS

FI - CLOR 60S
FI - CLOR 91

Fisons Ltd
Agrochemical Division
Harston
Cambridge
CB2 5HU

For this product the following condition applies:

A single application should not exceed 3 fl ozs per 1000 sq/ft
surface area.

VAPORIN

Wilkinson and Simpson Ltd
Low Friar Street
Newcastle-upon-Tyne
NE99 1LE

WHO INTERNATIONAL REFERENCE CENTRE FOR COMMUNITY WATER SUPPLY

Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Background document 4.2/3
Restricted

Statement on the toxicity of coagulant aids
(draft agenda item 4.2)

by

Dr. G. Stefanov
Centre of Hygiene
Sofia, Bulgaria

THE USE OF POLYELECTROLYTES IN WATER TREATMENT

Statement by Dr. G. Stefanov

The use of polyelectrolytes as flocculants or coagulants in the purification of potable waters has set many a problem from the toxicological point of view. As regards the basic problem relevant to the evaluation of the possible effects on health, it may be stated that the data available at the present do not give a definite answer, due to the lack of continuous and complex studies and observations in that respect.

In connection with this, special attention should be paid to some aspects determining the main lines and directions along which all future studies should proceed, namely:

1. Physico-chemical characteristics, connected mainly with the evaluation of the migration of water-soluble monomers depending on the different conditions and doses in the treatment of waters.

2. Toxicological Characteristics

2.1 The great variety of the polyelectrolytes used and the possibility of altering their toxicological characteristics upon changes occurring in each of the chemical bonds, makes imperative a concrete evaluation of each one of them.

2.2. In order to render possible a comparative evaluation of the observation data in the different countries, it is necessary to establish certain basic criteria and methods for their toxicological testing.

2.3 A great part of the polyelectrolytes permitted and used presently, should be considered as "conditionally innocuous" until we have established by efficient and sensitive biochemical and other tests data which point to possible adverse effects on human health.

2.4 Norms with regard to the residual quantities of monomers in the polyelectrolytes and in the water, should be set on the basis of complex and continuous observations.

2.5 The existence of a possible interrelation between the soluble monomers and some of the natural macro- and micro-components of the water should be thoroughly studied.

3. Elaboration and unification of the methods for efficient control of the production of electrolytes and their application in the treatment of water.

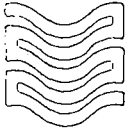
It is necessary in due course to standardize the polyelectrolytes which should be permitted for use.

On the other hand, the control methods for the presence of monomers in the water should be unified.

Efficient methods for the decrease and elimination of the soluble monomers should be established.

- - - -

The great variety and complexity of the problems to be solved makes imperative the preparation of a coordinated programme for their complex investigation and solution. Some of the problems presented in the present statement may be taken into consideration when preparing such a programme.



Expert Meeting on the Toxicity of uPVC pipes
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Proposed items for general discussion
of toxicity of coagulant aids
agenda item 4.3

4.3/1 Chemicals used in water treatment

- 1.1 Discussion and agreement on principles of limitation
- limit of residual monomer in water
 - limit of residual monomer in chemical
 - limit of polyelectrolyte residual
 - maximum permissible dose in water treatment
 - approval based on the condition of providing the used production scheme by the manufacturer

- 1.2 Organization and evaluation of toxicological test procedures
limits - daily intake

- 1.3 Analytical control of residuals

4.3/2 Delineation of tasks of national or international committees on the use of chemicals in water treatment

WHO INTERNATIONAL REFERENCE CENTRE FOR COMMUNITY WATER SUPPLY

Expert Meeting on the Toxicity of uPVC pipes
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Background document 5.2/1
Restricted

Statement on the toxicity of uPVC pipes
(draft agenda item 5.2)

by

National Sanitation Foundation
Ann Arbor, Michigan
U.S.A.

NATIONAL SANITATION FOUNDATION
STATEMENT ON
TOXICITY OF PVC DRINKING WATER PIPE

PREPARED FOR
COMMUNITY WATER SUPPLY
MEETING ON TOXICITY OF PVC PIPE
THE HAGUE
FEBRUARY 8 TO 12, 1973

1.0 INTRODUCTION

In the United States, plastic pipe is not approved for potable water applications when toxic stabilizers in excess of the maximum permissible levels (1) can be extracted under standard test conditions. As a result of this policy and data acquired during 10 years of testing the suitability of plastic pipe for drinking water transport, use of lead and cadmium stabilizers in plastics compounded for potable water applications has not been permitted since 1961. The long term effect of this decision has been the development of new super-activity tin stabilizers. These materials are economically competitive with lead stabilizers in terms of pipe raw material costs associated with their use. Secondary advantages provided by the super-activity tins would suggest that *all countries producing potable water pipe with toxic stabilizers should reassess their positions in this regard.*

2.0 STABILIZATION OF POLY-VINYL CHLORIDE (PVC) POTABLE WATER PIPE IN THE UNITED STATES

2.1 Background

PVC resins must be compounded with heat stabilizing chemicals for all commercial applications, including plastic pipe and fittings. These chemical additives protect the resin during high temperature processing into

pipe form as well as providing long term resistance to deterioration of the finished product.

Essential criteria for selecting the optimum stabilizer for use in plastic pipe for potable water applications include:

1. Health safety of ultimate potable water consumer
2. Health safety of personnel producing the pipe or compounds
3. Effects on appearance, taste and odor of potable water
4. Development and maintenance of maximum physical properties and aggressive chemical exposure resistance in the product
5. Cost contribution of stabilizer to finished pipe product cost.

In the United States, potable water pipe for both hot and cold water use is now being produced from PVC and CPVC without toxic additives and without any compromise in any of the criteria outlined above.

2.2 *Compound Preparation*

The most serious health hazard to production personnel occurs during the intensive mixer processing of powder type pipe compounds. Elimination of dust and exposure to airborne toxic lead particles is virtually impractical in this operation. The use of liquid, plasticizing tin stabilizers completely avoids this toxicity problem and in addition

significantly reduces the resin dust problem. The liquid form of stabilizer facilitates accurate metering of the critical level of stabilizer into each mixer charge. The plasticizing efficiency of the liquid tin stabilizer results in rapid absorption into the resin and effective distribution throughout the compound. It effectively prevents compound segregation in silo or conveying equipment which, is caused by specific gravity differential between resin and dry metallic salt stabilizers.

2.3 Compound Formulation

The ultimate goal of all PVC compounding is to achieve the required stability and processability with an absolute minimum of nonresin additives. This insures optimum physical properties, chemical resistance, and longest useful life expectancy.

Development of super-activity tin stabilizers in the past several years has effectively reduced the total stabilizer content of pipe compounds from 2 to 3% down to 0.3%. In addition to the direct benefits obtained in strength and uniformity of the plastic melt from this 10 fold reduction in concentration of a nonresin compound, a new degree of compounding freedom has been achieved. Interactions between lubricant or pigments or processing aid and the stabilizer have been minimized. Selection of type and amount of lubricant to tailor a compound to a specific extruder has become more certain. The pigments and processing

aids appear to be more effective in achieving a uniform, fluid plastic melt.

2.4 *Pipe Extrusion*

Until the past several years, essentially all PVC plastic potable water pipe in the U.S.A. has been produced on single screw extruders either in a high shear extrusion of powder mix or in a low shear extrusion of pre-mixed cubed compound. These extrusion operations were out of context with pipe making procedures in Europe and many other countries where twin screw production of pipe had been favored. The few cases where lead stabilized compounds were run on U.S. equipment for production of DWV pipe indicated a tendency toward brittleness problems due to overlubrication and melt in homogeneity. Part of the preference for twin screw extrusion equipment is undoubtedly due to the superior pumping and mixing efficiency of this type extruder under conditions of general overlubrication. The important fact to consider is that testing of pipe made under favorable conditions in Europe and in U.S.A., in spite of stabilizer and machinery differences, exhibited physical strength and long term stress testing predictions of ultimate useful life which are essentially identical.

Accepting the utility of single screw extruders for production of tin stabilized potable water pipe after some 15 years of optimization in the U.S. market, it is

still uncertain whether tin stabilized formulations can compete in all respects in the context of twin screw extrusion technology. Fortunately the demand for large diameter heavy wall pipe has resulted in a rapid introduction of European twin screw equipment in the U.S.A. during the past 5 years. A major portion of U.S. production is now being produced at high rates and with equivalent properties on twin screw extruders with a super-activity tin stabilizer base. In no case have problems developed which would lead one to expect difficulties in introduction of tin stabilizers to all world markets.

A direct comparison of European and U.S. resins and compounds was conducted on 4 inch and 6 inch SDR 21 pipe. All observations indicated complete interchangeability of resins and stabilizers when using this twin screw equipment, as shown in Appendix A.

Additional data are included in the reports, "Twin Screw Extrusion of Rigid PVC Pipe: II ADVASTAB[®] TM-181 versus Lead Stabilized Pipe - European Compounds, III ADVASTAB[®] TM-181 versus Lead Stabilized Pipe for European Markets, and IV TM-181 versus TM-181-S, T-31 Super", Appendix B.

3.0 TESTING OF PLASTICS FOR POTABLE WATER APPLICATIONS IN THE UNITED STATES

3.1 *NSF Standard Number 14 for Thermoplastic Materials, Pipe, Fittings, Valves, Traps, and Joining Materials*

Plastic pipe used for potable water applications in the U.S.A. is evaluated by the National Sanitation Foundation (NSF) to ensure conformance with NSF Standard 14 (2). The purpose of this standard is to establish the necessary public health and safety requirements for thermoplastic materials, pipe, fittings, and joining materials based on specific use and application, including potable water, and to provide for conditions and provisions of evaluation thereof.

3.2 *Supportive Research*

Development of Standard 14 was preceded by a three year study (3) undertaken at the request of the plastics industry, and mutually endorsed by leading health and water utility officials to determine the suitability of plastic pipe for use with potable water. Specific goals were to establish whether, a) any substances that might be deleterious to health would be extracted from the plastic by an aggressive potable water, and b) the passage of water through plastic pipe might effect the appearance, odor, or taste of the water.

The study began in 1952 under the sponsorship of the Society of the Plastics Industry for its Thermoplastic Pipe Division and suppliers of plastic materials. An advisory committee representing industry, regulatory and

user groups guided the study. Twenty-two samples of plastics most commonly used for conducting cold water, as well as proposed new formulations and a few plastics not recommended for use with potable water, were subjected to hundreds of chemical, organoleptic, and toxicological tests. Tin stabilized PVC pipe was included in the 22 samples.

Exposure and extraction techniques were established using aggressive water adjusted to pH 5.0 to simulate the most adverse conditions expected to exist in practice. Complete wet chemical and spectrophotometric analyses were performed on the extracted water after 72 hours of exposure to the plastics in a 100°F environment. Samples were agitated during incubation by inverting the sample containers ten times, three times daily. Taste, odor, and effects on chlorine residuals were also studied, using a recirculating system.

A final test of possible deleterious effects was made with colonies of Wistar Strain white rats for 18 months, the test animals drank only water that had been in prolonged contact with thermoplastics. Records of each animal's health during the study and autopsy reports prepared by pathologists showed no evidence of any deleterious effects attributable to extractants in the water.

3.3 NSF Program Evaluation and Listing

Basic extraction and testing procedures developed

during the three-year supportive research program are utilized today in the continuing evaluation and listing program at NSF. Contents of the standard are reviewed at intervals of not more than three years to maintain current and effective requirements consist with advancing technology. Analytical methodology is similarly reviewed and up-dated to provide better instrumentation and internal quality control in the testing program.

All samples to be evaluated at NSF are collected by NSF personnel, from manufacturing plants, warehouses, or points of installation on a random basis, at unannounced visits and intervals. Permission to use the NSF seal on plastic pipe for potable water applications is contingent upon demonstrated compliance with Standard Number 14.

To date, more than 20,000 samples of plastic pipe have been evaluated. These data are readily available for comparison with data for lead leached from lead stabilized pipe as referenced in Section 7.1 of the background paper prepared for this meeting.

NSF continues to be deeply concerned about health-safety requirements related to plastics for potable water applications. This concern is reflected in a paper presented by C. A. Farish before the American Chemical Society at its 158th National Meeting (1969). A copy of this paper is appended (Appendix C).

4.0 EXTRACTION OF LEAD FROM LEAD STABILIZED PVC PIPE

In September, 1970 the National Sanitation Foundation presented to WHO a report of a study undertaken by NSF at its own expense to determine the level of total extractable lead in lead stabilized PVC pipe, and to compare the analytical extraction method of the Water Research Association (4) (WRA) with the standard method employed by NSF. A copy of this report is attached as Appendix D. These data show clearly that lead in excess of the United States maximum permissible limit of 0.05 mg/l (1) can be extracted from lead stabilized PVC pipe through a relatively long series of extractions, using the British method.

5.0 NEED FOR ADOPTING EXPOSURE, EXTRACTION, AND ANALYTICAL PROCEDURES

From data shown in the NSF report, "Extraction of Lead from Lead Stabilized PVC Plastic Pipe" (Appendix D), and information contained in, "Plastics in Water Distribution Systems", (Appendix C), the need for adopting uniform standards for exposure, extraction, and analytical procedures for evaluating the toxicity of plastic pipe for potable water applications is clearly evident. Differences which currently exist between European and U.S. practices result in producing data which cannot be directly related. A thorough discussion of this subject at the Community Water Supply meeting and rapid resolution of these differences is deemed essential by NSF.

6.0 SUMMARY

It is well recognized by all concerned parties that the use of lead stabilizers for uPVC pipe intended for potable water applications does present a potential health hazard, not only to the compounder but to the ultimate consumer. While initially there was some economic justification for the use of lead stabilizers, the more recent development of super-activity tin stabilizers has negated this problem. Thus, it would seem most logical from a public health viewpoint to eliminate the use of lead or other toxic stabilization systems for uPVC pipe intended for potable water applications.

The adaptation of uniform exposure, extraction, and analytical procedures for evaluating toxic materials leached from PVC pipe for potable water applications is deemed essential.

References

1. "Drinking Water Standards," U. S. Public Health Service, 1962.
2. "Standard No. 14: Thermoplastic Materials, Pipe, Fittings, Valves, Traps, and Joining Materials", National Sanitation Foundation, Ann Arbor, Michigan, October 1965.
3. "A Study of Plastic Pipe for Potable Water Supplies", National Sanitation Foundation, Ann Arbor, Michigan, June 1955.
4. "Determination of the Total Soluble Lead Content of a uPVC Water Pipe," Water Research Association Technical Inquiry Report No. 183, July 1968.

APPENDIX A

COMPARISON OF EUROPEAN AND U.S. RESINS

	<u>4 inch SDR21</u>		<u>6 inch SDR21</u>	
	Cinn. AGM-CT-111/8 Corvic D 60/11		Cinn. AGM-CT-111/8 Geon 103 EPF-76	
Extruder				
Resin				
Stabilizer	2.4 lead	0.3 Tin	2.4 lead	0.3 Tin
Raw Matl. Cost (US \$)	.1240	.1237	.1240	.1237
Screw Speed (RPM)	19	19	19	19
Load (KW)	17	15	29	27
Output (lbs/hr)	500	475	610	660
Drop Impact (10 lb/6 ft)	ok	ok	ok	ok
Quick Burst (ATM)	61	61	--	--
Surface (plateout)	severe	none	none	none
Surface (smoothness)	rough	smooth	smooth	smooth

APPENDIX B

TWIN SCREW EXTRUSION OF RIGID PVC PIPE

II ADVASTAB[®] TM-181 VERSUS LEAD STABILIZED PIPE
EUROPEAN COMPOUNDS

H. Eigruber & G. A. Thacker

Presented at a Joint Cincinnati AGM
Cincinnati Milacron Chemicals Program
Linz, Austria, June 21, 1971

III ADVASTAB[®] TM-181 VERSUS LEAD STABILIZED PIPE
EUROPEAN MARKETS

IV TM-181 VERSUS TM-181-S, T-31 SUPER
G. A. Thacker

Presented at a Joint Cincinnati AGM
Cincinnati Milacron Chemicals Program
Oakley, Plant 4, August 23-31, 1971

(2)

II ADVASTAB[®] TM-181 versus Lead Stabilized Pipe

INTRODUCTION

A new generation of tin stabilizer technology has begun with the recent development and introduction of ADVASTAB[®] TM-181 by Cincinnati Milacron Chemicals. As rigid PVC pipe, profiles, sheet and moldings experience rapid growth in the construction, plumbing, packaging, appliance and transportation industries by displacing other materials, production and material cost requirements are becoming more and more critical.

ADVASTAB TM-181 has demonstrated the capability of delivering improved processing stabilization at costs 15-30% below classical dibutyltin bis isooctyl thioglycolate stabilizers in several U.S. rigid PVC markets: Pipe, conduit, sheeting, profile extrusion, injection molding. However, lead stabilized rigid PVC is more dominant in Europe and Japan. ADVASTAB TM-181 is the first tin stabilizer that can offer an advantage over lead on a cost-performance basis. Obvious other advantages for TM-181 include lower toxicity, better flow properties of molten rigid PVC, and freedom from plateout problems.

This report presents laboratory and extrusion data comparing the cost-performance of TM-181 and lead-stabilized pipe, which demonstrates that TM-181 offers a better alternative to lead stabilization.

I. TWIN SCREW EXTRUSION

A series of preliminary pipe extrusions carried out by Horst Eigruber in Linz Austria on an AGM CT 111/8 conical twin screw extruder compared the performance of several TM-181 stabilized formulations with a typical lead stabilized pipe compound.

Extruder: CT 111/8
 Screws: Standard
 Die Head: R-1714
 Die: .110 x 5.3 mm (4 inch SDR 21 pipe)

③

Formulation	Cost/lb. (U.S. Funds)				
	<u>XD5</u>	<u>XD6</u>	<u>XD6/1</u>	<u>XD 6/2</u>	
Corvic D-60/11 (K valve=60)	100	100	100	100	
K-120N	--	1.5	--	--	
TiO ₂	1.0	1.0	1.0	1.0	
Ca stearate	0.4	0.6	0.6	0.6	
Stearic acid	0.4	--	--	--	
165 paraffin wax	0.2	1.2	1.2	1.0	
Loxio1 G-30	0.1	--	--	--	
Pb sulfate	1.0	--	--	--	
Dibasic Pb stearate	1.0	--	--	--	
n-Pb stearate	0.4	--	--	--	
OMYA BSH	--	--	4.0	4.0	
AC 629A polyethylene	--	0.4	0.4	0.2	
ADVASTAB [®] TM-181	1.45	0.3	0.3	0.3	
	<hr/>	<hr/>	<hr/>	<hr/>	
	104.5 lbs.	105 lbs.	107.5 lbs.	107.1 lbs.	
Total cost (U.S. \$)	\$12.960	\$13.783	\$13.303	\$13.209	
RMC/lb. (U.S. \$)	\$.1240	\$.1310	\$.1237	\$.1234	
Output lbs/hr	480-500	480-500	475-490	440-480	
Compound bulk density g/l	560	540	550	546	

Pipe Quality

Drop impact, 10 lbs/6 ft.	ok	ok	ok	ok
Quick burst, ATM.	61	60	61	60
O.D. color, surface	Pink, grey, glossy	white, glossy	off-white, glossy	off white, glossy
I.D. color, surface	pink, grey severe plateout	white, smooth	off-white smooth	off-white, glossy
Specific Gravity:	88.3 lbs/ft ³	86.8 lbs/ft ³	88.6 lbs/ft ³	
Cost/ft ³ U.S.	\$10.94	\$11.37	\$10.96	

CONCLUSION:

TM-181 stabilized compounds furnished pipe showing superior appearance in surface and color, with comparable physical properties, output rates and formulation costs versus lead stabilized pipe.

II. Laboratory Static and Dynamic Testing

Pipe formulations XD5, XD6 and XD6-1 (using Geon 103 EP F-76 resin in place of Corvic D-60/11) were subjected to static oven and dynamic torque rheometer evaluations.

<u>Pipe Formulations</u>	<u>Static Oven, 380°F.</u> <u>1st color failure</u>		<u>Brabender</u> <u>210°C. 50rpm. 60g.</u>				<u>Plateout</u>
			<u>Fusion</u>	<u>Stability</u>			
			<u>Time</u>	<u>Torque</u>	<u>Time</u>	<u>Torque</u>	
XD5	10'	40'	17.4'	1675	7.4'	1700	
XD6	10'	25'	5.0	1950	4.4'	1575	
XD6-1	15'	30'	5.7	1575	4.5'	1350	

CONCLUSIONS:

XD5, the lead stabilized formulation exhibits better long term static color stability than XD6 or XD6-1 and also better dynamic processing stability - - both results being inconsistent with the pipe extrusion results. One answer is the extremely lubricating nature of the lead compound (17.4' to fusion!) which diminishes the frictional heat accumulation on the two roll mill or in the brabender chamber. XD6-1, a lower cost TM-181 stabilized compound than XD6, furnished slightly better static and processing stability with lower peak and minimum torques than XD6. This will translate to slightly lower power requirements for a given output rate.

RECOMMENDATION:

Additional pipe extrusion trials should be carried out on the CT 111/8 in Oakley, further refining the cost-performance comparison of TM-181 versus lead stabilized pipe. Hopefully these results will reinforce the Linz data, adding to our confidence in approaching the European rigid PVC (especially pipe) markets.

##



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE June 21, 1971

EXTRUDER: CT 111/3

Company: European Pipe Market

Screws: Standard

Formulation: XDS (Lead stabilized) type I grade I

Die Head: R-1714

Bulk Density: 560 g/l Mixing: _____ min. to 230 °F.

Die: 110x5.3 mm (4"SER 21)

Brabender Stability: _____ minutes @ _____ °F. _____ RPM (Melt torque 4750 m²/s)

Feed: Starve feeder

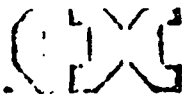
Fusion: 36% 10' minutes @ 320 °F. 60 RPM

FORMULATION	No.	XDS				
Time		4:00 p.m.				
Screw speed	RPM	19				
Load	kWp/kW	17				
Back Pressure	Tons	16.0				
Starve Feeder	RPM	43				
Vent Vacuum	mm	600				
<u>Temperature Profile</u>						
Zone 1	} Barrel	°F.	340			
Zone 2		°F.	355			
Zone 3		°F.	320			
Zone 4		°F.	275			
Zone 5 Adapter		°F.	320			
Zone 6 Spider		°F.	349			
Zone 7 Die I		°F.	353			
Zone 8 Die II		°F.	410			
Zone 9 Mandril		°F.	410			
Zone 10		°F.				
Zone 11		°F.				
Zone 12		°F.				
Zone 13		°F.				
Zone 14		°F.				
Screw Off		°F.	300			
Output Rates	lbs/hr	500				
	Ft./min					
<u>Product Quality</u>						
Drop Wgt. Impact 1/2" IAD.	ft/lbs	6' / 10' ok				
Quick Burst	psi	39				
Acetone/methylene chloride	/	ok / ok				
O.D. Color. surface		1. creas-				
I.D. Color. surface		4th. with				

pipe-platcoat

Comments

Compound exhibited severe platcoat - otherwise ran ok.



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE June 21, 1971

EXTRUDER: CT 111/3

Company: European Pipe Market

Screws: Standard

Formulation: XP-6 tin-with E120N-type I Grade I

Die Head: R-1714

Bulk Density: 56.0 g/ml Mixing: min. to 230 °F.

Die: 110x5.3mm(4" SDR21)

Brabender Stability: minutes @ °F. RPM (Melt torque 4600 mdy)

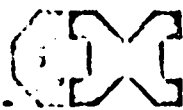
Feeds:

Fusion: 36.7 minutes @ °F. 60 RPM

FORMULATION	No.	XP6	XP6	XP6		
Time		10:45	12:00	12:30		
Screw speed	RPM	19	18.8	18.8		
Load	Amps	14	18	18		
Back Pressure	Tons	13	18	17		
Starve Feeder	RPM	minimum	43	43		
Vent Vacuum	mm	-	-	675		
<u>Temperature Profile</u>						
Zone 1	°F.	320	310	330		
Zone 2 } Barrel	°F.	330	330	330		
Zone 3 } Barrel	°F.	310	310	310		
Zone 4 } Barrel	°F.	300	285	285		
Zone 5 Adapter	°F.	320	340	340		
Zone 6 Spider	°F.	350	355	355		
Zone 7 Die I	°F.	375	383	383		
Zone 8 Die II	°F.	383	392	392		
Zone 9 Mandril	°F.	375	392	392		
Zone 10	°F.					
Zone 11	°F.					
Zone 12	°F.					
Zone 13	°F.					
Zone 14	°F.					
Screw Oil	°F.	300	293	293		
Output Rates	lbs/hr ft./min	-	493	498		
<u>Product Quality</u>						
Drop Wgt. Impact 1/2" KAD	ft/lbs			6"/10" ok		
Quick Burst	psi			BRU		
Acetone/methylene chloride	/			o.d. - ok		
O.D. Color, surface				I.D. Sl. craze		
I.D. Color, surface				white - no other flaws		

Comments

Compound exhibits good flow - slight die line marks on I.D.



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE June 21, 1971

EXTRUDER: CT 111/8

Screws: Standard

Die Head: R-1714

Die: 110x5.3mm(4"SDR21)

Feeds: Starve Feeder

Company: European Pipe Market

Formulation: XD6/1 tin-no K120N-type I grade I

Bulk Density: 550 g/Mixing: _____ min. to 330 °F.

Brabender

Stability: _____ minutes @ _____ °F. _____ RPM (Melt Torque

Fusion: 36g 12' minutes @ 320 °F. 60 RPM 4300 m/f)

FORMULATION	No.	XD61	XD61	XD61		
Time		1:15	2:00	2:45		
Screw speed	RPM	19	19	19		
Load	Amps/KW	15	16	16		
Back Pressure	Tons	15	17	17		
Starve Feeder	RPM	43	43	43		
Vent Vacuum	mm	530	670	670		
<u>Temperature Profile</u>						
Zone 1	°F.	330	345	345		
Zone 2	°F.	350	355	355		
Zone 3	°F.	310	320	320		
Zone 4	°F.	295	275	275		
Zone 5	°F.	335	320	320		
Zone 6	°F.	355	375	375		
Zone 7	°F.	385	385	385		
Zone 8	°F.	392	400	400		
Zone 9	°F.	392	400	400		
Zone 10	°F.					
Zone 11	°F.					
Zone 12	°F.					
Zone 13	°F.					
Zone 14	°F.					
Screw Off	°F.	300	300	300		
Output Rates	lbs/hr ft./min	—	475	475		
<u>Product Quality</u>						
Drop Wgt. Impact	ft/lba			6 1/10	ok	
Quick Burst	psi			89	ok	
Acetone/ethylene chloride	/					
O.D. Color, surface					off white, glossy	
I.D. Color, surface					off white, smooth	

Comments

Compound runs quite good - excellent pipe, although not pure white.

PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE 6/21/71

EXTRUDER: CT 111/8
 Screws: Standard
 Die Head: R-1714
 Die: 110x5.3 (4" SDR 21)
 Feeds: Starve feeder

Company: European Pipe Market
 Formulation: XD6/2 tin - no k120n, lower lubricant type I Grade I
 Bulk Density: 546 g/l Mixing: _____ min. to 230 °F.
 Brabender
 Stability: _____ minutes @ _____ °F. _____ RPM (Melt torque 4700 m/g)
 Fusion: 36g, 10' minutes @ 320 °F. 60 RPM

FORMULATION	No.	XD6/2			
Time		3:00			
Screw speed	RPM	19			
Load	Kdps/KW	19			
Back Pressure	Tons	19.5			
Starve Feeder	RPM	43			
Vent Vacuum	mm	620			
<u>Temperature Profile</u>					
Zone 1	°F.	345			
Zone 2 Barrel	°F.	355			
Zone 3	°F.	320			
Zone 4	°F.	275			
Zone 5 Adapter	°F.	320			
Zone 6 Spider	°F.	350			
Zone 7 Die I	°F.	335			
Zone 8 Die II	°F.	400			
Zone 9 Mandril	°F.	395			
Zone 10	°F.				
Zone 11	°F.				
Zone 12	°F.				
Zone 13	°F.				
Zone 14	°F.				
Screw Oil	°F.	300			
Output Rates	lbs/hr ft./min	440-480			
<u>Product Quality</u>					
Drop Wgt. Impact	ft/lbs	6'/10' ok			
Quick Burst	psi	880			
Acetone/ethylene chloride	/	ok/ok			
O.D. Color. surface		off-white-glossy			
I.D. Color. surface		off-white-glossy			

Comments

Lower lub. level creates more work, greater frictional heat which contributed to higher load, back pressure, & high gloss I.D. Pipe is excellent quality - although not pure white.

III ADVASTAB[®] TM-181 versus Lead Stabilized Pipe

and

IV TM-181 versus TM-181-S, T-31 Super

A. Purpose & Scope of Project

III. TM-181 versus Lead Stabilized Pipe for European Markets

A continuation of the trials begun in Linz, June, 1971 (see report II) would reinforce and add to those preliminary findings that low-cost TM-181 stabilized pipe compounds can compete with lead stabilized pipe in both EEC and EFTA countries of Europe.

Through the use of a very low level of TM-181 stabilizer, minimal use of pigments, processing aids, and an efficient lubricant system, several tin formulations were developed to be cost competitive with typical European style lead formulations. The purpose of these extrusion runs was to determine if these tin formulations were also performance competitive to the lead compounds. The comparison was made between Leads I & II, and Tins III, IV, V and VI.

B. Conclusions

III. Tin versus Lead

To the extent that the Lead I and Lead II compounds truly represent actual European practice, our low cost tin compounds III, IV, V and VI are more than capable of competing on a cost-performance basis with lead pipe compounds of Europe. Pipe of at least equivalent quality and appearance was obtained at equivalent or higher output rates. This, coupled with lower toxicity and freedom from plateout, clearly spells out the advantage of TM-181 stabilized pipe over lead stabilized pipe.

European compounding practice avoids the use of acrylic processing aids (K-120N), which is reflected in Tins IV, V. Tins III and VI contain the acrylic, and could be of interest to the U. S. pipe market since they represent an additive cost of 1.67¢ and 1.18¢ over resin cost respectively.

Lead I ran well but required higher temperatures than the tin compounds to achieve adequate fusion. Even at the higher

temperatures, the lead did not have the hot strength of the tins - run at lower temperatures.

Lead II was totally inadequate - being both underlubricated and understabilized. Adjustment of external lubrication is required.

C. Experimental Conditions

Compound Preparation: All pipe compounds were mixed in a high intensity Littleford Rotoplast mixer (W 600) and cooled in a Littleford K 1200 cooling mixer. Each formulation was based on 1000 pounds of PVC and four 250 pound resin charges were mixed for each compound. In each case, resin process aids, pigment and stabilizer were mixed at high speed to 215°F at which point the lubricants were added and high speed mixing continued to 230°F (110°C) drop temperature.

The time required to attain 230°F drop temperature was noted and generally averaged between 5 and 6 minutes. Bulk density was determined for each mix upon cooling to 90-100°F.

Extrusion: A Cincinnati AGM conical twin screw extruder, CT 111/8 was equipped with a starve feeder, an R-22 die head and a 6" SDR 21 pipe die for these runs. The extruder contained a set of BL200/S pipe screws featuring a progressive lead in the metering zone, which results in essentially at 1:1.1 compression ratio.

The pipe line was strung up using an external calibrating sleeve to achieve O.D. surface and a floating plug with internal air pressure to achieve proper sizing.

Pipe cooling was achieved initially with cascade water followed by water spray.

With all formulations except Lead II, the extruder was run at maximum screw RPM (19-20) and the starve feeder adjusted to flood feed the screw flights with powder. Maximum output rates were sought for each compound, consistent with maintaining pipe quality.

Excellent output rates of 620-655 pounds/hour were obtained. Therefore, 1000 pounds of compound lasted only about one and a half hours which did not permit time to make fine adjustments at the die to achieve exact wall thickness.

D. Pipe Compound Cost Considerations

All compound RMC's were generated using \$0.12/pound for PVC resin cost. The lead stabilizer costs represent rock-bottom European pricing. The actual selling price of leads is somewhat higher, so we purposely stack the deck against tins.

Tin stabilizer prices of \$1.45/pound do not reflect the recent large volume \$1.35/pound contract price. This would make the tin formulations even more attractive versus lead. For example, Tin IV at \$0.1237 RMC would be reduced to \$0.1215 RMC using the \$1.35 price for TM-181.

All other formulation ingredients are priced either at the U. S. level (which is not too different from Europe, according to Horst Eigruber) or at the European price if it was known.

E - LEAD AND CMC TIN STABILIZED TWIN SCREW PIPE FORMULATIONS

	<u>Cost/ Lb. \$</u>	<u>Lead I</u>	<u>Lead II</u>	<u>Tin III</u>	<u>Tin IV</u>	<u>Tin V</u>	<u>Tin VI</u>
Geon 103 EP-F76	.12	100	100	100	100	100	100
K-120N (acrylic)	.40	-	-	1.5	-	-	0.5
TiO ₂	.25	1.0	1.0	1.0	1.0	0.5	0.5
Ca Stearate	.29	0.4	0.315	0.6	0.6	0.6	0.6
St. Acid	.18	0.4	-	-	-	-	-
165 Wax	.17	0.2	-	1.2	1.2	1.2	1.2
GMS (140 Wax)	.21	-	0.355	-	-	-	-
Loxio1 G-30	.36	0.1	0.23	-	-	-	-
Pb Sulfate	.174	1.0	0.7	-	-	-	-
Dibasic Pb Stearate	.199	1.0	0.625	-	-	-	-
γ-Pb Stearate	.199	0.4	-	-	-	-	-
Omya BSH	.03	-	1.0	-	4.0	3.0	2.0
AC 629 A PE	.30	-	-	0.4	0.4	0.4	0.4
Advastab TM-181	1.45	-	-	0.3	0.3	0.3	0.3

Compound Wgt.	Lbs.	104.5	103.2	105.0	107.5	105.8	105.3
RMC \$/Lb.		.1240	.1220	.1310	.1237	.1235	.1258
Bulk Density	Lbs./Ft. ³	39.6	38.25	38.5	39.0	38.75	38.20
CT 111/8 Output	Lbs./Hr.	590-630	500	620	655	655	650

F. Results of Specific Extrusion Runs

Lead I is a typical European lead stabilized pipe compound that, in Horst Eigruber's view, represents current formulation practice in Europe. This formulation carries a 12.40¢ compound RMC and is the yardstick against which the low-cost tin formulations are compared. Pipe of excellent quality was obtained but the run appeared to require more operator attention - - - - mechanical difficulties resulted in a broken line twice, principally due to the lack of hot strength of the compound (tears easily). Although this run was hotter than the tin runs (for fusion requirements), it probably should have been run at still higher temperatures. No plateout was experienced during this short run, although the same compound exhibited severe plateout when run in Linz. Satisfactory output rates of 590-630 pounds/hour were obtained.



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE 8/31/71

EXTRUDER: CT111/8
 Screws: BL200/S
 Die Head: R-22
 Die: 6" SDR .21
 Feed: Starve

Company: CMC
 Formulation: Lead I (Eigruber's)
 Bulk Density: 39.6 Mixing: 5'24" min. to 230° °F.
 Brabender (60g)
 Stability: 7.4 minutes @ 410 °F. 50 RPM Torque 1700
 Fusion: 17.4 minutes @ 410 °F. 50 RPM 1675

FORMULATION	No.				
Time		12:15		1:00P.M	
Screw speed	RPM	19-20		19-20	
Load	Amps	28-30		28-30	
Back Pressure	Tons	14-15		13-14	
Starve Feeder	RPM	4.8		4.8	
Vent Vacuum Kp/Cm ²	mm	0.68		0.4	
<u>Temperature Profile</u>			Requires more heat for fusion than tin blends.		Line broke - - not too much hot strength
Zone 1	°F.	350		350	
Zone 2	°F.	360		360	
Zone 3	°F.	355		355	
Zone 4	°F.	355		355	
Zone 5 Adapter	°F.	365		350	
Zone 6 Spider	°F.	370		370	
Zone 7 Die I	°F.	385		385	
Zone 8 Die II	°F.	360		360	
Zone 9 Mandrel	°F.				
Zone 10	°F.				
Zone 11	°F.				
Zone 12	°F.				
Zone 13	°F.				
Zone 14	°F.				
Screw Oil	°F.	330	330		
Output Rates	lbs/hr Ft./min	630		592	
<u>Product Quality</u>					
Drop Wgt. Impact	ft/lbs				
Quick Burst	psi				
Acetone/methylene chloride	/				
O.D. Color. surface	V.S.L. Grey-white-glossy			White-glossy (V.S.L. Grey cast)	
I.D. Color. surface					

Comments 12:30 Line lost - water got inside pipe - cooled pipe at die & it tore open.
 1: P.M. Excellent O.D. output down to 592 lbs. line broke when hauloff didn't close properly.

Lead II a formulation obtained from Holland was a disaster. Hints of trouble were seen in the quick fusion, high torque Brabender runs. Having quick fusion similar to a tin compound, this formulation was extruded initially using a temperature profile similar to the tin runs. However, no fusion was evident at the vent and temperature settings were increased. The machine was running slowly (10RPM) but before temperatures could increase sufficiently to create a melt in the die head, the back pressure increased to 40 tons, and the die head bolts blew off!!!

A second attempt at considerably higher temperatures and at slow speed (10-11RPM) furnished very high machine amperage (load, or torque on screws), but back pressure was satisfactory. The compound began to burn at the vent, and yellow, poor quality pipe was obtained. This formulation is underlubricated and understabilized, at a compound RMC of 12.20¢/pound but should not be considered further. Output rate was not determined, but believed to be well below 500 pounds per hour at this slow speed.



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE 8/25/71

EXTRUDER: CT 111/8
 Screws: BL 200/S
 Die Head: R-22
 Die: 6" SDR 21
 Feed: Starve

Company: CMC
 Formulation: Lead II (van Dorn's)
 Bulk Density: 38.25 lb/ft³ Mixing: 5'4" min. to 230 °F.
 Brabender
 Stability: _____ minutes @ _____ °F. _____ RPM
 Fusion: _____ minutes @ _____ °F. _____ RPM

FORMULATION	No.	Start			Repeat 8/31/71 Start	
Time		9:20			1:15	
Screw speed	RPM	9-10			12-13	
Load	Amps	20 $\xrightarrow{\text{sudden to}}$ 40			40	
Back Pressure	Tons	16 $\xrightarrow{\text{sudden to}}$ 30-40			14-15	
Starve Feeder	RPM	2			2.8	
Vent Vacuum	mm	-			none	
<u>Temperature Profile</u>						
Zone 1	°F.	340	Die bolts blew out at 30 tons!!		350	Compound under-lubricated & under stabilized; two rear zones had to be heated too much to induce fusion-power brown (tan) at vent.
Zone 2	°F.	355			370	
Zone 3	°F.	335			360	
Zone 4	°F.	320			360	
Zone 5 Adapter	°F.	320			355	
Zone 6 Spider	°F.	360			340	
Zone 7 Die I	°F.	340			370	
Zone 8 Die II	°F.	350			385	
Zone 9 Mandril	°F.	350			360	
Zone 10	°F.					
Zone 11	°F.					
Zone 12	°F.					
Zone 13	°F.					
Zone 14	°F.					
Screw Oil	°F.	295			330	
Output Rates	lbs/hr Ft./min				less than 500	
<u>Product Quality</u>						
Drop Wgt. Impact	ft/lbs					
Quick Burst	psi					
Acetone/methylene chloride	/					
O.D. Color. surface					Yellow-burn line	
I.D. Color. surface					Yellow-glossy	

8/25/71 Too cold-melt extremely stiff.

Comments 8/31/71 - Line broke from lead II run-hauloff didn't close, machine slowed to 10-11 RPM-still running very high load (AMPS)-after 15 min. a yellow burn started at spider-compound yellow overall-no hot strength-line broke again.

Tin III is a low cost Type I Grade I pipe compound utilizing a very low stabilizer level (0.3 phr- TM-181) and a lubricant system previously evaluated for the CT 111/8 machine. This compound contains an acrylic processing aid, and closely represents current U. S. pipe compounding practice. Carrying an RMC of 13.1¢/pound, Tin III furnished excellent pipe at a very good output of 620 pounds/hour, having a high gloss, white outside diameter and a very smooth interior. This compound was used as a standard against which the other tin stabilized compounds were compared.



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE 8/23/71

EXTRUDER: CT 111/8

Company: CMC

Screws: Pipe-Progressive Lead Formulation: Tin III (TM-181, K 120 N)

Die Head: R-22 BL 200/S Bulk Density: 38.5 Lbs/Mixing: 5 min. to 230 °F.

Die: 6" SDR 21.

Brabender (60g.) Stability: 4.4 minutes @ 410 °F. 50 RPM Torque 1575

Feed: Starve

Fusion: 5.0 minutes @ 410 °F. 50 RPM 1950

FORMULATION	No.	StringUp				
Time		11:10 AM		11:40	12:15	
Screw speed	RPM	19-20 Top		19-20	20	
Load	Amps	32		32	31	
Back Pressure	Tons	17-18		15	15	
Starve Feeder	RPM	5		5	5	
Vent Vacuum Kp/cm ²	mm	0.71		0.71	0.69	
<u>Temperature Profile</u>						
Zone 1	°F.	335	String Up went smooth - Inside slightly cool - Up Mandril and Die Temp.	335	335	Very Smooth Run
Zone 2	°F.	360		360	360	
Zone 3	°F.	320		320	320	
Zone 4	°F.	315		315	315	
Zone 5 Adapter	°F.	315		318	320	
Zone 6 Spider	°F.	375		380	380	
Zone 7 Die I	°F.	338		350	350	
Zone 8 Die II	°F.	362		370	370	
Zone 9 Mandril	°F.	345		355	365	
Zone 10	°F.					
Zone 11	°F.					
Zone 12	°F.					
Zone 13	°F.					
Zone 14	°F.					
Screw Oil	°F.	295-300	295	290		
Output Rates	lbs/hr	581		618	620	
	Ft./min	3.33		3.33	3.50	
<u>Product Quality</u>						
Drop Wgt. Impact	ft/lbs					
Quick Burst	psi					
Acetone/methylene chloride	/				White - Glossy	
O.D. Color. surface					White - Smooth	
I.D. Color. surface						

Comments 11:40 - Excellent O.D. - Rate - GOOD I.D.

Tin IV is a lower cost version of Tin III by virtue of a stearate treated calcium carbonate filler (BSH) replacing the more costly acrylic processing aid. This compound carries a 12.37¢/pound RMC. Tin IV ran extremely well delivering a 655 pound/hour output at a slightly lower back pressure and screw load (amperage) than Tin III. A small increase in temperature was necessary to achieve adequate fusion. This behavior confirms the lower peak and fusion torques seen on the Brabender Plastograph for Tin IV.



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE 8/24/71

EXTRUDER: CT 111/8
 Screws: BL 200/S
 Die Head: R-22
 Die: 6" SDR 21
 Feed: Starve

Company: CMC

Formulation: Tin IV (TM-181, BSH)

Bulk Density: 39 Mixing: 7.5 min. to 230 °F.

Brabender

Stability: 4.5 minutes @ 410 °F. 50 RPM

Fusion: 5.7 minutes @ 410 °F. 50 RPM

Torque

1350

1575

FORMULATION	No.	Start with Tin				
Time		8:45 ^{Run}	10:00		11:00	
Screw speed	RPM	8	19-20		19-20	
Load	Amps	15	28		26	
Back Pressure	Tons	10	15		14	
Starve Feeder	RPM	1.5	4.8		4.8	
Vent Vacuum kp/cm^2	mm	-	0.67		0.67	
<u>Temperature Profile</u>						
Zone 1	°F.	345	325	Not holding round - cold - spider lines on O.D.; compound not as fused at vent - running smoothly, but needs more heat - rear zones increased, also Die I.	340	Trouble was with crooked plug! This straightened, plus higher temps. gave excellent high gloss pipe, once on size.
Zone 2	°F.	370	360		380	
Zone 3	°F.	330	320		335	
Zone 4	°F.	310	320		335	
Zone 5	°F.	315	320		330	
Zone 6	°F.	370	380		385	
Zone 7	°F.	350	350		365	
Zone 8	°F.	370	370		370	
Zone 9	°F.	365	365		365	
Zone 10	°F.					
Zone 11	°F.					
Zone 12	°F.					
Zone 13	°F.					
Zone 14	°F.					
Screw Oil	°F.	295-300	290-295	295		
Output Rates	lbs/hr Ft./min		665		655	
<u>Product Quality</u>						
Drop Wgt. Impact	ft/lbs					
Quick Burst	psi					
Acetone/methylene chloride	/					
O.D. Color. surface					White-Glossy	
I.D. Color. surface					White-Smooth	

Comments Excellent output rate! Needs slightly higher temperature for adequate fusion - very smooth running.

Tin V represents a further attempt at cost reduction (RMC 12.35¢/pound) being identical to Tin IV except that the pigment level (TiO_2) was cut in half and the filler (BSH) was reduced. Again, this compound ran very smoothly at low load and back pressure, delivery excellent quality pipe at high output, 655 pounds/hour. The reduction in TiO_2 content resulted in an off-white color, but surface gloss on the outside and smoothness on the inside remained excellent. As with Tin IV, this compound had to be run at slightly higher temperatures than Tin III to insure adequate fusion.

Tin VI contains a very low level of acrylic processing aid, low pigment and filler levels - - a compromise between Tin III and Tin V. With a compound RMC of 12.58¢/pound, Tin VI furnished excellent quality pipe at a 650 pound/hour rate. Slightly off-white due to low pigment level, Tin VI exhibited a tendency to quicker fusion, noticeable at the vent, which is what would be expected with the use of an acrylic process aid. Low amperage and low back pressure characterized this run also.



PLASTICS PROCESSING LABORATORY

EXPERIMENTAL EXTRUSION REPORT

DATE 8/24/71

EXTRUDER: CT 111/8

Screws: BL200/S

Die Head: R-22

Die: 6" SDR 21.

Feed: Starve

Company: CMC

Formulation: Tin VI (TM-181, BSH/K120N)

Bulk Density: 38.2 Mixing: 5'25" min. to 230 °F.

lb/ft³
Brabender

Stability: _____ minutes @ _____ °F. _____ RPM

Fusion: _____ minutes @ _____ °F. _____ RPM

FORMULATION	No.				
Time		12:45		1:30	
Screw speed	RPM	19-20		19-20	
Load	Amps	26		26	
Back Pressure	Tons	13		13	
Starve Feeder	RPM	4.8		4.8	
Vent Vacuum Kp/Cm ²	mm	0.67		0.68	
<u>Temperature Profile</u>			Very easy running cpd - fusion just beginning at vent.		
Zone 1	°F.	340		345	
Zone 2	°F.	375		375	
Zone 3	°F.	340		340	
Zone 4	°F.	330		330	
Zone 5 Adapter	°F.	330		330	
Zone 6 Spider	°F.	385-390		390	
Zone 7 Die I	°F.	360		360	
Zone 8 Die II	°F.	370		370	
Zone 9 Mandril	°F.	365		365	
Zone 10	°F.				
Zone 11	°F.				
Zone 12	°F.				
Zone 13	°F.				
Zone 14	°F.	290-		290-	
Screw Oil	°F.	295	295		
Output Rates	lbs/hr Ft./min	655		650	
<u>Product Quality</u>					
Drop Wgt. Impact	ft/lbs				
Quick Burst	psi				
Acetone/methylene chloride	/				
O.D. Color. surface				Off-White-Glossy	
I.D. Color. surface				Off-White-Smooth	

Comments

A little Kizon is noticeable in Sl. quicker fusion-seen at vent. Excellent output - very easy run.

PLASTICS IN WATER DISTRIBUTION SYSTEMS

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National Sanitation Foundation
Ann Arbor, Michigan

Presented at the 158th National Meeting
American Chemical Society
New York, N.Y.
September 7-12, 1969

*Executive Director

INTRODUCTION

Plastics are, by definition, "materials, generally of high molecular weight and of intricate molecular complexity, whose form and/or properties may be transformed into useful shapes or articles by the technique of applying heat, pressure, or other manufacturing procedures"(1). They are generally divided into two basic groups: thermoplastics and thermosets. Nearly all of those used in potable water applications are thermoplastics; i.e., they are materials which can be softened by heating and reset by cooling without undergoing chemical change.

The unique physicochemical properties which permit plastics to be tailor-made for a given application have contributed largely to the phenomenal growth of the industry. Plastic piping was first used in Europe in 1930 and in the United States in 1940. In recent years, it has assumed a major role in potable water transportation. More than 200,000 miles of plastic pipe and fittings are now in domestic service. Among its numerous advantages are its light weight; high strength; easy, economical installation; and excellent corrosion resistant properties. Ex- and infiltration are eliminated by chemically welded joints made of nonabsorbant materials.

No other single commodity is more important to the health and well-being of man than his supply of potable water. It must be of high quality, unimpaired by the distribution system which delivers it for his ultimate use. In 1951, state health officials became concerned about transporting potable water in pipes made of plastic. They expressed their concern through the Conference of State Sanitary Engineers and the American Water Works Association.

On the recommendation of these two professional organizations, representatives of the plastics industry requested that the National Sanitation Foundation study the suitability of plastics for underground use in conveying potable water supplies. The Foundation was selected for this undertaking because of its recognized objective concern for matters pertaining to the health and well-being of man.

NSF

This is the twenty-fifth anniversary year of the National Sanitation Foundation (NSF), a not-for-profit, non-official agency dedicated to research, education, and service in all areas concerned with man's health and environment. It serves as a "neutral" medium, bringing together the interests of business and industry, official regulatory agencies, and the public in programs of mutual concern.

Early activities of the Foundation were directed toward standards development for food service equipment. Manufacturers and national distributors of these items were plagued by the multiplicity of rules, regulations, codes, and laws under which they were required to operate. Frequently, large engineering and clerical staffs were retained in order to comply with requirement variations in the 28,000 or more regulatory jurisdictions throughout the United States. Equipment destined for a specific locality had to be modified to meet the public health "preferences" of that community. Health significance was frequently overlooked in order to meet the preferences of an individual inspector. This problem was recognized by leaders in public health and industry and the Foundation was asked to develop a methodology for establishing uniform, nationally accepted standards based on facts, sound engineering, and fundamental

principles. As a result, representatives of all concerned groups were brought together to: (1) study the problem, (2) define the need, (3) outline the necessary research, and (4) establish uniform, nationally accepted requirements for these products.

This mechanism has been utilized in the development and implementation of thirty-six standards or criteria for food service equipment or products, wastewater treatment devices, swimming pool water treatment equipment and chemicals, radiation monitoring devices, and plastic pipe. Requests for the initiation of a new program at the Foundation may come from health officials, industries, users, or combinations of these three groups. Products for which standards have not yet been developed are submitted for research and preliminary tests of performance capability.

PLASTICS RESEARCH ACTIVITIES AND STANDARDS DEVELOPMENT

At the request of the plastics industry, a three-year research program was initiated at the Foundation in 1951. The purpose of this study was to determine whether any deleterious substances would be extracted from plastic pipe by an aggressive potable water, and whether the water's appearance, taste, or odor would in any way be affected by its passage through the pipe. Financial support for the study was provided by a grant from the plastics industry.

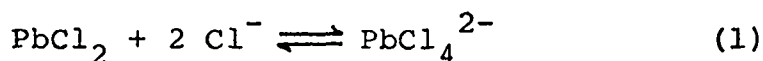
In keeping with the policy of NSF, representatives of all interested groups were invited to serve as advisers to the project. Under the guidance of this "Advisory Committee," a testing protocol was developed.

Toxicological and Organoleptic Considerations

Elements such as lead, cadmium, strontium, lithium, and antimony can be used in plastics formulations as stabilizers,

substances which prevent the aging of polymers. The limits stated in the U.S. Public Health Service's Drinking Water Standards (2) for these and other physical, chemical, biological, and radiological characteristics are now generally accepted as minimum quality standards for water at the free-flowing outlet of the ultimate consumer.

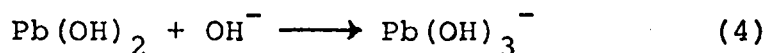
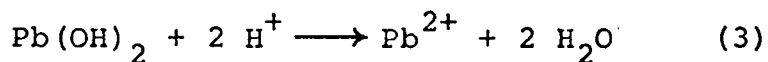
According to this document, the acceptable upper limits for lead and cadmium, two potential stabilizers, are 0.05 and 0.01 milligram per liter, respectively. All soluble lead salts are toxic. They act as cumulative poisons because their elimination, which is through the kidneys, is very slow. Even small concentrations of lead continuously present in the drinking water may cause serious illness or death. Lead poisoning is not normally a problem with hard water because of the insoluble nature of lead carbonate (PbCO_3) and lead sulfate (PbSO_4). Lead chloride (PbCl_2), however, is slightly soluble in water and readily soluble in hot water. In the presence of high concentrations of chloride ions, tetrachloroplumbate ions (PbCl_4^{2-}) are formed:



If oxygen is present, lead reacts with water to form lead hydroxide (Pb(OH)_2):



The hydroxide will dissolve under acid conditions or in the presence of excess alkali, as shown in the following two reactions:



Cadmium accumulates in the soft tissues of the body, resulting in anemia, poor metabolism, arterial changes in the liver, and at high concentrations, death.

To represent the most adverse field conditions, water, adjusted to pH 5.0, was exposed to various plastic compounds for 72 hours at a temperature of 100°F. At the end of this period, the appearance, taste, and odor of the water were evaluated. Wet chemical and spectrographic techniques were used to identify and quantify any toxic substances extracted into the water. Lead in concentrations greater than 0.05 milligram per liter was extracted from a number of samples of lead stabilized plastic pipe during this study.

Further toxicological evaluations were made by bioassay, using colonies of Wistar Strain white rats. For 18 months, the test animals drank only water that had been in prolonged contact with thermoplastic compounds while their health was observed and recorded. At the end of this period, the animals were sacrificed and autopsies performed. No evidence was found of damaging effects which could be attributed to compounds in the water they consumed.

Publication of the report, "A Study of Plastic Pipe for Potable Water Supplies" (3) marked the end of the plastics research program and the beginning of standards development and testing services to assure the continuing public health safety of plastic compounds used in potable water applications. Knowledge gained from the research program was used as the basis for performance evaluation services, initiated in 1959.

Physical Requirements

It soon became apparent that physical standards, as well as toxicological and organoleptic (taste and odor) considerations, were vitally important in an effective testing program. Whenever applicable standards or criteria are available from other recognized sources, they are utilized and appropriately referenced in an NSF standard. Commercial Standards (C.S.) and Product Standards (P.S.) of the U.S. Department of Commerce, American Society for Testing and Materials (ASTM) Standards and Test Procedures, and United States of America Standards Institute (USASI) Standards were adopted by the Foundation for defining the physical requirements of plastic pipe. Another physical standard is currently being developed by the American Water Works Association (AWWA) Plastics Pipe Standards Committee. When it becomes available, the Foundation will also include this standard in its testing program.

NSF STANDARD 14

Standard Number 14, "Thermoplastic Materials, Pipe, Fittings, Valves, Traps, and Joining Materials" (4), was published by the National Sanitation Foundation in October 1965. The requirements set forth in this document are those which are considered to be the minimum conditions necessary to insure the continued protection of the public's health and safety. This Standard, like all NSF documents, was reviewed by the Council of Public Health Consultants. Members of this Council represent public health expertise from all levels of government. They are elected to serve on the Council on the basis of professional recognition and competence in the field of public health. When the

Council of Consultants recommends that a standard or criteria be adopted, it is referred to the Foundation's Board of Trustees. This group provides the official ratification for the document, and authorizes its publication, distribution, and use in NSF evaluation and listing programs. The names of persons currently serving on the Board of Trustees and the Council of Public Health Consultants, and copies of all NSF standards and criteria are available from the Foundation on request.

POTABLE WATER PIPE MATERIALS

There are many thermoplastic materials which can be used for producing plastic pipe but only five are in general use for pressure rated potable water installations:

(1) Acrylonitrile-Butadiene-Styrene (ABS) is a copolymer blend or a terpolymer of the ingredients from which it gets its name. It is semi-rigid in relation to metal, but is classed as rigid among thermoplastics. It is available in black or shades of gray, in straight lengths. Acrylonitrile is a colorless liquid used as an ingredient in producing buna-type synthetic rubber. Butadiene and styrene are also used in producing certain types of synthetic rubber. In combination, these three make a plastics material which has excellent properties.

(2) Polyethylene (PE) is made by the polymerization of ethylene. This pipe is capable of being coiled and ranges in flexibility from flexible to semi-rigid. Polyethylene pipe incorporates an ultraviolet attenuator, such as carbon black. Originally made only in flexible low density form, it is now available as low, medium, and high density materials.

(3) Polyvinyl Chloride (PVC) is a polymer of vinyl chloride. It is a semi-rigid pipe which is manufactured in various colors and shades. It offers the combined features of high strength, toughness, excellent chemical resistance, and resistance to weathering.

(4) Chlorinated Polyvinyl Chloride (CPVC) is now being produced for use in hot water applications.

(5) Polybutylene (PB) was first introduced in 1965. It combines the flexibility of conventional polyethylene with the properties of high strength, outstanding resistance to cold flow and environmental stress cracking, toughness, and good wear. It is used for heavy duty down well pipe and water service tubing.

PERFORMANCE EVALUATION AND LISTING SERVICES

The National Sanitation Foundation Testing Laboratory (NSFTL) is a not-for-profit wholly owned subsidiary of the Foundation, organized to conduct health related research, evaluate and test the performance of equipment and products for compliance with NSF standards, and to govern and control the use of the NSF seal. Seal programs are self-supporting through charges made for testing and listing services.

Each plastics manufacturer who requests that a product be evaluated under Standard 14 must submit to the Foundation complete formulation information for the product. This information permits the staff to determine which tests will be performed. The formula is filed in a security vault and retained on a confidential basis. Samples for physical, toxicological and organoleptic evaluation are selected on a random basis during an NSF representative's unannounced visit to the manufacturer's plant. Retesting is performed annually,

or more frequently if it is deemed necessary, to insure compliance with the Standard. All pipe found to conform with the Standard is authorized to carry the NSF seal. This insignia is your assurance that the pipe is non-toxic, will not adversely affect the appearance, taste, or odor of the water, and that it conforms with the applicable physical standards to which it is produced and identified. At this moment, 220 companies are authorized to use the NSF seal under Standard 14.

CURRENT TRENDS

The plastic pipe used in Europe for potable water applications varies somewhat from that which is used in the United States. Size is one of these variations. In the European countries, diameters range up to 40 inches. By contrast, the largest diameter pipe used in this country is 16 inches. This practice may soon be changed, however. Production of larger pipe sizes is currently being considered by several American manufacturers.

Perhaps the major difference at home and abroad is in the stabilizers which can be used in potable water pipe. Lead stabilized pipe has been used extensively in Europe and in the Orient, with no associated public health problems recorded. The only stabilizers accepted for use in the United States are those which permit no extraction of toxic elements greater than the limits expressed in the Drinking Water Standards (2). In this country, the risk of lead exposure from sources other than drinking water is relatively high. Automobile exhaust emissions contribute to the level of lead in the atmosphere. Food ingestion may also contribute to the total intake of this potentially toxic element.

Recent research activities in England and in the Netherlands have been designed to measure the concentrations of

"total soluble lead" in lead stabilized pipe. These studies, conducted by the Water Research Association (WRA, England) and the Institution for the Testing of Water Works Materials (KIWA Ltd., the Netherlands) have been supported by the World Health Organization (WHO). Through discussions with members of the staff of WRA, a copy of the experimental procedure was obtained. The methodologies used by the WRA for pipe exposure and extraction of soluble lead are different from those which are used by NSF. A comparative study was initiated at NSF to determine the significance of these differences. Using lead stabilized PVC pipe prepared for the study by an American manufacturer, exposures were made using the WRA method and the standard procedure of the NSFTL. The extractant used by WRA has a pH of approximately 1.1. Lengths of pipe are cut to size, filled with a measured volume of extractant, closed with rubber stoppers covered with polyethylene film, and agitated at room temperature on the apparatus shown in Figure 1. At the end of one hour, the concentration of lead in the extractant is measured by emission spectroscopy.

The extractant used by the NSFTL is Ann Arbor tap water which has been adjusted to pH 5.0 with CO_2 . Sections of pipe are placed in Pyrex, ground glass stoppered bottles and held in contact with the extractant for three days at 100°F . The concentration of lead in the extractant is again measured by emission spectroscopy.

After a series of exposures using each of these techniques, the data were compared. In all cases, the total soluble lead extracted from the sample pipe exceeded the limit of 0.05 milligram per liter defined by the Public Health Service as the maximum acceptable limit for drinking water.

This comparative study is being continued by NSF, but data acquired to date do not support the use of lead stabilized plastic pipe for transporting potable water.

CONCLUSIONS

The plastics industry is still growing rapidly. Existing compounds are continually being modified to improve their performance capabilities, and new products are concurrently being developed. Household plumbing applications will be expanded with the availability of plastic pipe which is safe and suitable for hot water delivery. It is the policy of the National Sanitation Foundation to keep pace with these developments by:

(1) providing a complete review of all existing standards at intervals not to exceed three years, and (2) conducting on-going research activities designed to up-date its testing program. Through its efforts, the manufacturer, the regulatory official, and the consumer can be assured that plastic pipe which bears the NSF seal is public health safe for distributing potable water.

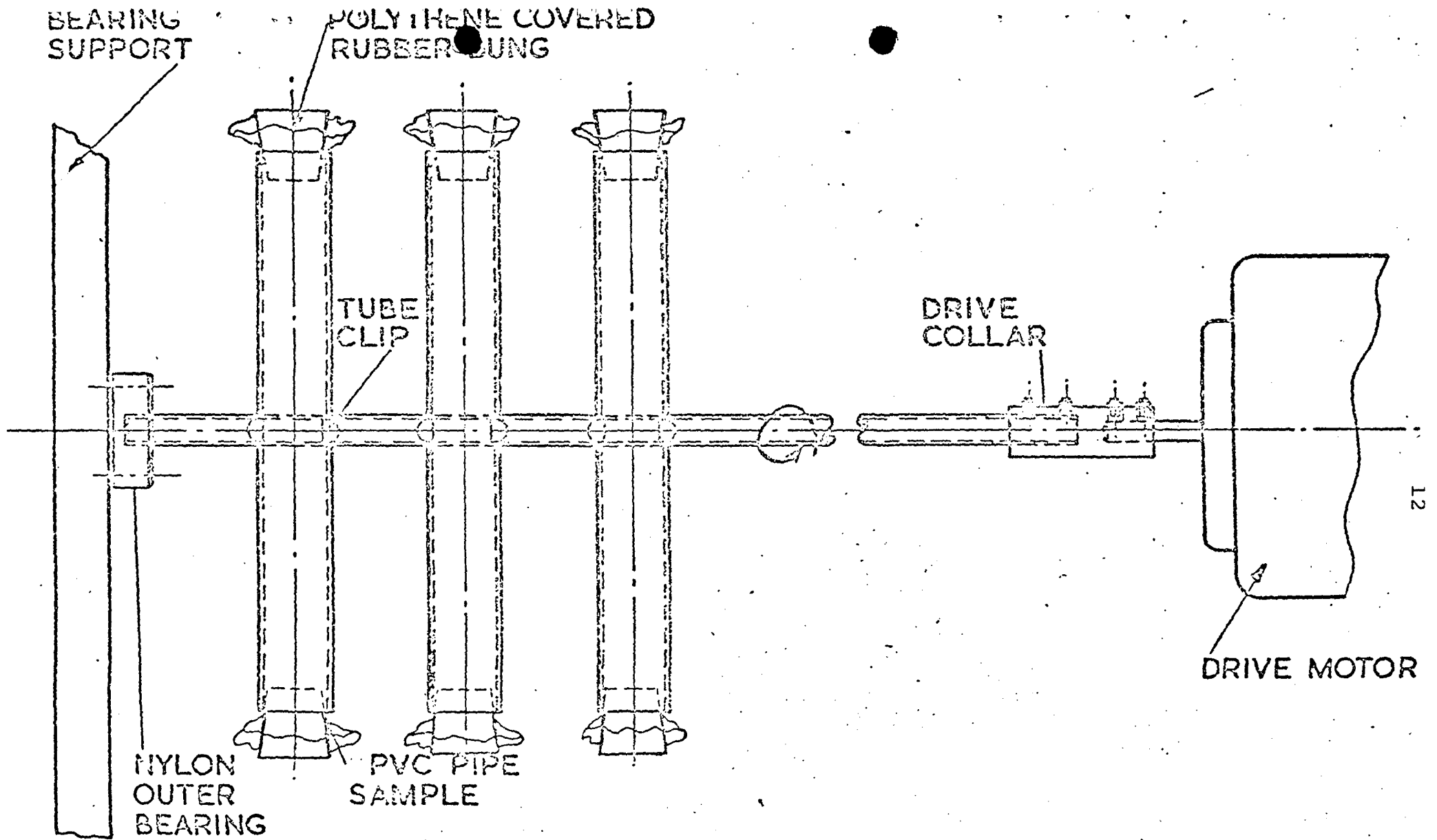


FIG. I. APPARATUS USED IN LEAD EXTRACTION TESTS

REFERENCES

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APPENDIX D

EXTRACTION OF LEAD FROM
LEAD STABILIZED PVC PLASTIC PIPE

National Sanitation Foundation Testing Laboratory

Ann Arbor, Michigan

September 1970

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Introduction

In a recent report developed under the sponsorship of the World Health Organization (WHO), the Water Research Association (WRA) reviewed the use of stabilizers in polyvinyl chloride plastic (PVC) pipe (1). It is stated in this report that, "lead stabilizers are by far the most widely used in the fabrication of uPVC water pipe."

Standard No. 14 of the National Sanitation Foundation (NSF) (2) relates to plastic pipe used for potable water applications. The National Sanitation Foundation Testing Laboratory (NSFTL) evaluates plastic pipe used in the United States and certifies its conformance with the Standard. When toxic stabilizers in excess of the maximum permissible limits (U.S. Public Health Service, "Drinking Water Standards," 1962) (3) are extracted under standard test conditions, the pipe is not approved.

Lead tends to be deposited in the bone as a cumulative poison. Prolonged ingestion even at relatively low levels (varying with individual sensitivity) can result in serious illness or death. It can enter the body through food, air, tobacco smoke, and water and other beverages. The most prevalent source of lead in drinking water is that used in service piping or distribution systems.

In 1961, Niklas and Meyer (4) reported that "the extractable lead in a uPVC pipe is confined to a surface film which rapidly becomes removed as the pipe is flushed out." Sections of pipe were filled with water and allowed to stand. Most of the lead was reported to be given off in the first two or three days, with little change reported after 10 to 15 days. Migration of lead from the bulk of the pipe was said to take place only very slowly if at all. These investigations related extractable lead to the total initial content of lead in the pipe and concluded that, "only uPVC with a lead content of 1% or less should be employed in pipes to be used for the conveyance of drinking water."

WRA, in its Technical Inquiry Report (TIR) No. 183 dated 11 July 1968 (5) also stated that, "A high proportion of the total lead content of a lead stabilized uPVC pipe cannot be leached out by water passing through the pipe. A relatively small proportion however can be so leached and this is present in a film or layer on the inner wall of the pipe rather than in the bulk of the pipe material."

An analytical method for determining the "total soluble lead content" of lead stabilized PVC pipe was described in TIR 183. Using this method, the total soluble lead content of pipe made to B.S. 3505 (6) by four manufacturers was reported as follows, with each result the mean of three tests (TIR 183, Table 1):

TABLE I

"Results of Determination of Total Soluble Lead On 1 Inch Nominal Bore uPVC Pipes to B.S. 3505"

Pipe Manufacturer	Total Soluble Lead, ug cm^{-2}	Results of B.S. 3505 Extraction Test			
		Lead Content, mg/l First Extraction	Third Extraction	Total Lead Removed in Three Extractions, ug cm^{-2}	% of Soluble Lead Recovered
S	0.72	0.16	0.07	0.22	30
T	1.43	0.60	0.03	0.59	41
U	2.55	0.83	0.18	1.06	42
V	0.54	0.33	0.06	0.35	64

It is important to note that three of the four samples included in the data shown for the third extraction in "Table 1" above were greater than the maximum permissible limits (0.05 mg/l) defined by the U.S. Public Health Service "Drinking Water Standards." One of the four exceeded the maximum allowable limit of WHO "International Standards for Drinking Water" (7) (0.1 mg/l) and the tolerance limit of WHO "European Standards for Drinking Water" (8) (0.1 mg/l).

Purpose

The purpose of this paper is to present the data obtained by NSFTL in a study designed to determine the level of total extractable lead in lead stabilized PVC pipe, and to compare the analytical extraction method of WRA with the standard method employed by NSFTL.

Methodology

The two methodologies (WRA and NSFTL) for extracting soluble lead are summarized in Table II.

Results

Samples of 1-1/4 inch I.D. PVC plastic pipe obtained from a domestic (USA) manufacturer were used in a preliminary study. This pipe was typical of lead stabilized PVC pipe produced for drain, waste and vent (DWV) applications in the U.S. Results of twenty exposures in conformance with both methods (British & NSFTL) are shown in Table III. Because of the larger diameter pipe used in the preliminary study, the volume of extractant used for the British method of exposure was adjusted so that one-half of the total available volume of each pipe section was filled with extractant.

Note: In this paper, all data reported for exposures made in accordance with the British method were obtained by pooling the extractions from five sections of pipe. Three spectrographic determinations are run on each of the pooled samples. Reported values are arithmetic means of the three determinations.

From Table III, it can be calculated that a total of 86.2 ug of lead was extracted in 20 hours of exposure following the British method. Variations that occur throughout the entire series of observations suggest that lead may migrate from the bulk of the pipe over a prolonged interval. After 20 exposures by the British method, the level of lead extracted from the pipe was significantly greater than the U.S. maximum permissible limit - by about one order of magnitude. After six extractions by the NSFTL method - 18 days of exposure - the concentration of lead was greater than the maximum permissible (U.S.).

To complete this investigation, two sets of 1" I.D. pipe reported to be produced in conformance with British Standard (B.S.) 3505 - 1966 PVC Class E uPVC were obtained from a British manufacturer. Lead extractions were made from each of these samples, following both the British and NSFTL methodologies. In the tabulation of data which follows (Tables IV thru VI), these samples are identified as X and Y. Sample X was grey pipe, wrapped, and identified as " '(Trade Name' Class 3500.'" (Note: The class identification may not have been read properly. Numbers were not clear.) Sample Y was grey pipe, unwrapped, physically soiled, and unidentified. In Table IV, the results of twenty-one exposures are shown for Sample X. Similar data, obtained with Sample Y, are shown in Table V. With both samples, the time for the twenty-first exposure in the British method was extended to two hours, and in the NSFTL method, to 6 days. Following the British method, the level of lead in the twenty-first extraction of Sample X (22 hours of exposure) was still about 4 times higher than the U.S. maximum permissible limit.

Data shown in Tables IV and V were taken from 23 October through 2 December 69, a period of 41 days. Samples were analyzed only as time permitted; thus there were times between runs when the pipe samples were allowed to dry, then refilled. Following the twenty-first exposure, all pipe samples were air dried and stored at ambient temperatures for approximately nine months. Data from a recent series of exposures are shown in Table VI.

In studying the kinetics of toxic stabilizers leached from plastic pipe, the importance of considering long term data cannot be overemphasized. Data presented in Table IV for Sample X exposed according to the NSFTL standard method suggest that most of the 'soluble' lead is extracted in the first three exposures. Recent data, however, (Table VI) do not support this

assumption. Additional exposures will be made.

Conclusions

To date, results of the NSF study on "Extraction of Lead From Lead Stabilized PVC Plastic Pipe" do not support the theory that extractable lead is confined to a film on the inner wall of the pipe and migration from the bulk is of little concern. The U.S. Public Health Service Bureau of Water Hygiene recently studied the water supply systems of 989 communities serving 18.2 million people. In the report of this study (9), it was stated that, "Out of 900,000 persons being served potentially hazardous water (exceeding mandatory 1962 Public Health Service limits), 360,000 were drinking water with evidence of excess lead from pipes in the home or supply system." NSF's position with respect to approving for potable water applications no plastic pipe from which toxic stabilizers can be extracted in excess of the U.S. maximum permissible level will remain firm.

TABLE II
SUMMARY OF EXTRACTION TECHNIQUES

Variable	British (WRA) Method	NSFTL Method
Extractant	0.5% (v/v) nitric acid (HNO ₃) plus 0.85% (v/v) perchloric acid (HClO ₄) in double distilled water. pH ≈ 1.1	Ann Arbor tap water reduced to pH 5.0 with carbon dioxide (CO ₂) pH = 5.0
Procedure	<p>Test pipe is cut into 12" lengths (10" exposed; 2" for end closures). One end of each length of pipe is closed by a rubber stopper covered by polyethylene (PE) film.</p> <p>100 ml of extractant is added to each length of pipe - 1/2 the total available volume of the pipe section. The other end of pipe is tightly closed (rubber stopper covered by polyethylene film).</p> <p>Each length of pipe is clipped to a steel shaft for agitation at 30 rpm at room temperature. (Figures 1 and 2).</p> <p>After one hour of exposure, the lead content of the extractant is measured.</p> <p>Fresh extractant is added to the pipe lengths, and agitation is resumed.</p> <p>This procedure is followed through a series of exposures.</p>	<p>Test pipe is cut into 6" lengths and split longitudinally.</p> <p>Pipe sections are placed in Pyrex, ground glass stoppered bottles and incubated with extractant at 100°F for three days. Agitation is provided by shaking the bottles twice daily.</p> <p>After three days, the extractant is decanted and filtered through paper. Fresh extractant is added.</p> <p>This procedure is followed through a series of exposures.</p>
Surface Area of Pipe Exposed per Volume of Extractant	314 in ² /liter	250 in ² /liter

TABLE II (continued)

Variable	British (WRA) Method	NSFTL Method
Control	PE film equivalent in surface area to the end covers for all pipe sections is exposed to extractant in a Pyrex Erlenmeyer flask. Conditions of exposure are equivalent to those for test pipe sections except for agitation. Lead is measured.	Extractant is incubated in Pyrex container under conditions similar to those for test pipe sections. Lead is measured.
Extraction pre-treatment	5 ml concentrated HNO ₃ is added to 500 ml extraction. The volume is reduced to approximately 10 ml on a steam bath, then made up to 25 ml with double distilled water.	5 ml concentrated HNO ₃ is added to 500 ml extraction. The volume is reduced to approximately 15 ml on a steam bath, then made up to 50 ml with double distilled water.
Lead Determination	Colorimetric using dithizone. Note: <u>All</u> lead determinations run by NSFTL and reported in this paper - regardless of extraction methodology - were done by emission spectroscopy.	Emission spectroscopy.

TABLE III

Results of Preliminary Study Using U.S. PVC Plastic Pipe

Extraction No.	British Method - Pb, mg/l Sample	Control	NSFTL Method - Pb, mg/l Sample	Control
1	4.40	0.04	1.20	<0.05
2	0.80	0.045	0.25	<0.05
3	0.60	0.06	0.25	<0.05
4	0.40	0.03	0.16	<0.05
5	0.60	<0.025	0.16	<0.05
6	0.60	<0.025	0.14	<0.05
7	0.60	<0.025	0.07	<0.05
8	0.50	<0.025	0.05	<0.05
9	0.92	<0.025	0.07	<0.05
10	1.04	<0.025	0.06	<0.05
11	0.78	<0.025	0.06	<0.05
12	0.90	<0.025	0.08	<0.05
13	0.50	<0.025	0.08	<0.05
14	0.50	<0.025	<0.05	<0.05
15	0.40	<0.025	0.06	<0.05
16	0.70	<0.025	<0.05	<0.05
17	0.50	0.18	<0.05	<0.05
18	0.90	0.08	0.05	<0.05
19	1.00	0.03	<0.05	<0.05
20	0.60	<0.025	<0.05	<0.05

TABLE IV

Sample X - Results From 21 Exposures

Extraction No.	British Method		NSFTL Method	
	Sample X Pb, mg/l	Control Pb, mg/l	Sample X Pb, mg/l	Control Pb, mg/l
1	4.0	<0.03	0.40	<0.05
2	0.60	<0.03	0.10	<0.05
3	0.20	<0.03	0.10	<0.05
4	0.20	<0.03	<0.05	<0.05
5	0.10	<0.03	0.05	<0.05
6	0.15	<0.03	0.10	<0.05
7	0.20	<0.03	<0.05	<0.05
8	0.20	<0.03	0.05	<0.05
9	0.20	<0.03	0.05	<0.05
10	0.25	<0.03	0.05	<0.05
11	0.10	<0.03	<0.05	<0.05
12	0.10	<0.03	<0.05	<0.05
13	0.10	<0.03	<0.05	<0.05
14	0.20	<0.03	<0.05	<0.05
15	0.10	<0.03	<0.05	<0.05
16	0.10	<0.03	<0.05	<0.05
17	0.30	<0.03	<0.05	<0.05
18	0.10	<0.03	<0.05	<0.05
19	0.10	<0.03	<0.05	<0.05
20	0.20	<0.03	<0.05	<0.05
21	0.20*	<0.03	0.10**	<0.05

* 2 hours
exposure

** 6 days
exposure

TABLE V

Sample Y - Results From 21 Exposures

Extraction No.	British Method		NSFTL Method	
	Sample Y Pb, mg/l	Control Pb, mg/l	Sample Y Pb, mg/l	Control Pb, mg/l
1	0.60	<0.03	<0.05	<0.05
2	0.10	<0.03	<0.05	<0.05
3	0.10	<0.03	<0.05	<0.05
4	0.10	<0.03	<0.05	<0.05
5	0.10	<0.03	<0.05	<0.05
6	0.05	<0.03	<0.05	<0.05
7	<0.03	<0.03	<0.05	<0.05
8	0.05	<0.03	<0.05	<0.05
9	0.10	<0.03	<0.05	<0.05
10	0.03	<0.03	<0.05	<0.05
11	0.05	<0.03	<0.05	<0.05
12	0.05	<0.03	<0.05	<0.05
13	<0.03	<0.03	<0.05	<0.05
14	0.10	<0.03	<0.05	<0.05
15	0.10	<0.03	<0.05	<0.05
16	0.10	<0.03	<0.05	<0.05
17	0.10	<0.03	<0.05	<0.05
18	0.10	<0.03	<0.05	<0.05
19	0.10	<0.03	0.05	<0.05
20	0.10	<0.03	<0.05	<0.05
21	0.03*	<0.03	<0.05**	<0.05

*2 hours
exposure** 6 days
exposure

TABLE VI

Extraction No.	British Method				NSFTL Method			
	Sample X Pb, mg/l	Control Pb, mg/l	Sample Y Pb, mg/l	Control Pb, mg/l	Sample X Pb, mg/l	Control Pb, mg/l	Sample Y Pb, mg/l	Control Pb, mg/l
22	0.15	<0.03	<0.03	<0.03	0.44	<0.05	<0.05	<0.05
23	0.18	<0.03	<0.03	<0.03				
24	0.08	<0.03	<0.03	<0.03				

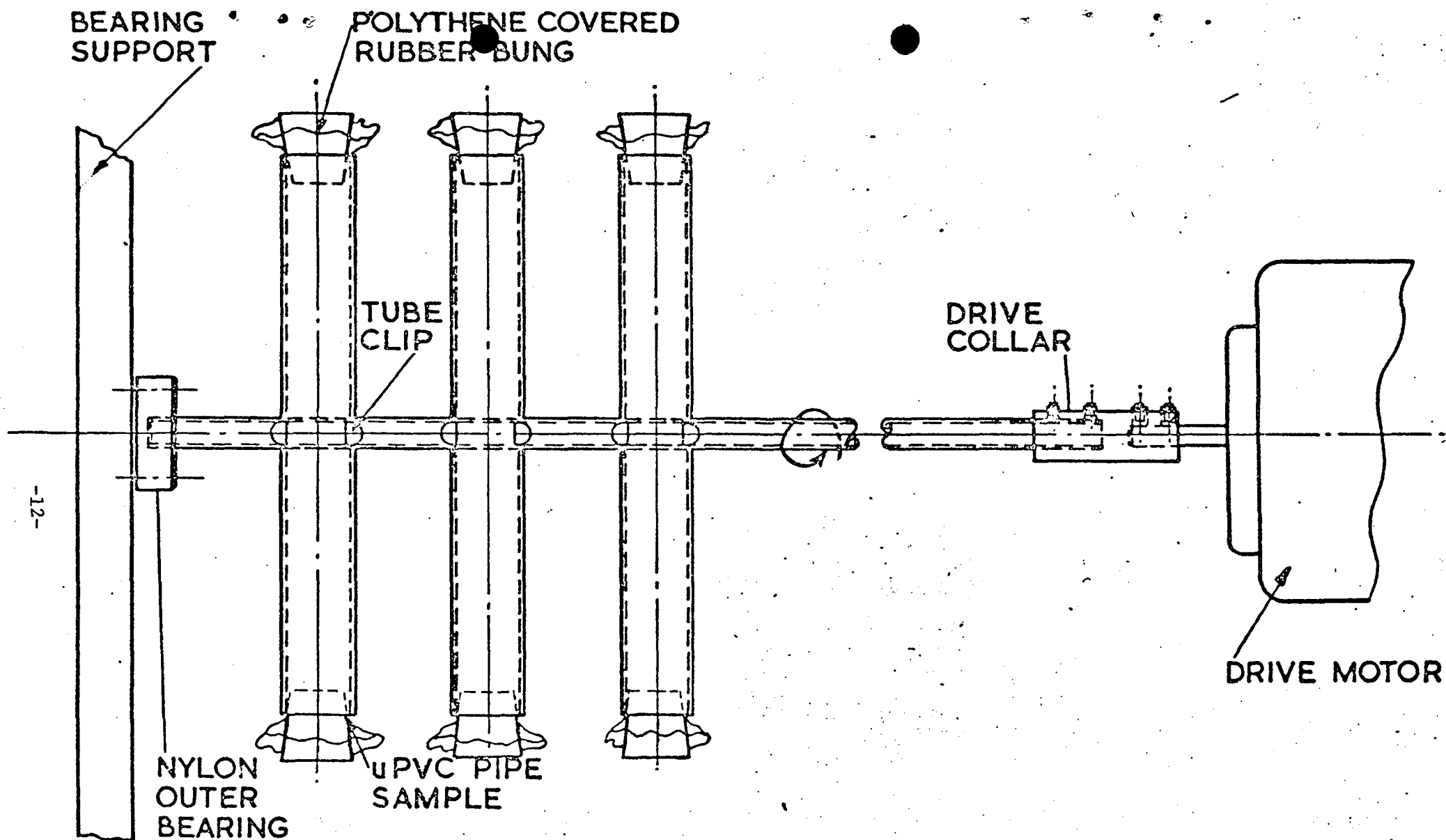


FIG. I. APPARATUS USED IN LEAD EXTRACTION TESTS ON uPVC PIPE SAMPLES

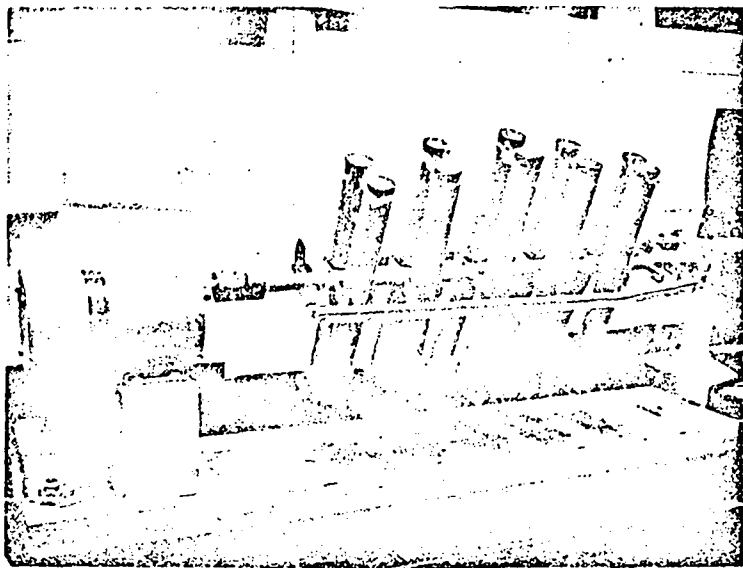


Figure 2

Photograph of apparatus used by NSF and shown schematically in Figure 1.

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2. "Standard No. 14: Thermoplastic Materials, Pipe, Fittings, Valves, Traps, and Joining Materials", National Sanitation Foundation, Ann Arbor, Michigan, October 1965.
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WHO INTERNATIONAL REFERENCE CENTRE FOR COMMUNITY WATER SUPPLY

Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Background document 5.2/2
Restricted

Statement on the toxicity of uPVC pipes
(draft agenda item 5.2)

by

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Toxicity of uPVC Drinking-Water Pipes

Statement of Dr. V. Benes

Drinking-water plastic pipes are of toxicological importance so long as their use results in elimination or at least decrease of the content of usual microquantities of toxic substances in drinking water. Substitution, for example, of polyethylene pipes for lead pipes satisfies this requirement (soot being usually allowed to be used as stabilizer). When using uPVC pipes stabilized with lead compounds, it is especially the migration of lead into drinking water that must become centre of interest from the toxicological point of view.

It results from the working background paper (C.H.I. Elzenga) that the concentration of lead leached from uPVC pipes into drinking water decreases with time as verified by experimental data. Values as far as 10 times lower than those of the lead concentration found hitherto in drinking water may be expected when uPVC pipes are substituted for lead ones. Apart from the initial enhanced migration relative decrease of the lead intake from drinking water may be taken in consideration.

For practical purposes it would be desirable to determine experimentally the period of initial leaching of the enhanced lead content from new uPVC pipes and recommend pertaining measures with the view of reducing the lead body burden to minimum as result in from drinking water. Even an effective washing out of uPVC pipes before their installation might be taken in consideration. The necessity of the use of uPVC pipes stabilized with lead for drinking-water supply must be, however, absolutely substantiated.

Toxicological evaluation of the hazard of microquantities of che-

mical substancies from oral intake of man (for example in food) is effected according to the concept of the ADI (acceptable daily intake) by WHO/FAO expert groups for many years. For cumulative heavy metals such as lead, mercury and cadmium a new approach was needed in view of considerations of the Joint FAO/WHO Expert Committee on Food Additives (Wld Hlth Org.techn.Rep. Ser.,1972,Nº 505). In case of lead the Committee established a provisional tolerable weekly intake of 3 mg of lead per person, equivalent to 0.05 mg/kg of body weight. This level applies to adults only without bearing to infants and children. The problem of environmental contamination with lead, mercury and cadmium is regarded as serious and it was generally recommended to reduce such contamination at all possible stages. The requirement should be generally accepted not to use cadmium compounds in production of uPVC pipes so far as migration of cadmium into drinking water is possible. From the toxicological point of view it is absolutely reasonable, according to the present state of our knowledge, to prevent any increase of the general background.

So far as the use of organo-tin stabilizers in uPVC pipes is concerned, the usual procedure of establishing ADI for evaluation of the risk of microquantities leached into drinking water may be recommended.

For residues of fungicidal fentin compounds (hydroxide, acetate and chloride) an ADI for man of 0.0005 mg/kg of body weight was set (Wld Hlth Org.techn.Rep. Ser.,1970,Nº 474).

Similarly, it would be highly desirable to evaluate, at international level of the WHO, the risk of microquantities of dialkyl tin compounds used or designated for use as stabilizers for uPVC pipes.

In the same way it is necessary to add that data for inorganic tin so far available do not permit establishment of a formal ADI. The dietary maximum level of tin is unknown. Extensive human experience alone does not indicate existence of any general acute toxicity ha-

zard (WHO Food Additives Series No 1, WHO Geneva 1972).

As to the possibility of migration of some organic substances from uPVC, their follow-up by means of currently used methods for water quality may be recommended. Although the problem of lead migration is of first rate importance, introduction of additional tests for these substances into the KIWA and WRA programs may be considered desirable.

WHO INTERNATIONAL REFERENCE CENTRE FOR COMMUNITY WATER SUPPLY

Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Background document 4.2/3

Restricted

Statement on the toxicity of coagulant aids

(draft agenda item 4.2)

by

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Centre of Hygiene
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THE USE OF POLYELECTROLYTES IN WATER TREATMENT

Statement by Dr. G. Stefanov

The use of polyelectrolytes as flocculants or coagulants in the purification of potable waters has set many a problem from the toxicological point of view. As regards the basic problem relevant to the evaluation of the possible effects on health, it may be stated that the data available at the present do not give a definite answer, due to the lack of continuous and complex studies and observations in that respect.

In connection with this, special attention should be paid to some aspects determining the main lines and directions along which all future studies should proceed, namely:

1. Physico-chemical characteristics, connected mainly with the evaluation of the migration of water-soluble monomers depending on the different conditions and doses in the treatment of waters.

2. Toxicological Characteristics

2.1 The great variety of the polyelectrolytes used and the possibility of altering their toxicological characteristics upon changes occurring in each of the chemical bonds, makes imperative a concrete evaluation of each one of them.

2.2. In order to render possible a comparative evaluation of the observation data in the different countries, it is necessary to establish certain basic criteria and methods for their toxicological testing.

2.3 A great part of the polyelectrolytes permitted and used presently, should be considered as "conditionally innocuous" until we have established by efficient and sensitive biochemical and other tests data which point to possible adverse effects on human health.

2.4 Norms with regard to the residual quantities of monomers in the polyelectrolytes and in the water, should be set on the basis of complex and continuous observations.

2.5 The existence of a possible interrelation between the soluble monomers and some of the natural macro- and micro-components of the water should be thoroughly studied.

3. Elaboration and unification of the methods for efficient control of the production of electrolytes and their application in the treatment of water.

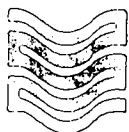
It is necessary in due course to standardize the polyelectrolytes which should be permitted for use.

On the other hand, the control methods for the presence of monomers in the water should be unified.

Efficient methods for the decrease and elimination of the soluble monomers should be established.

- - - -

The great variety and complexity of the problems to be solved makes imperative the preparation of a coordinated programme for their complex investigation and solution. Some of the problems presented in the present statement may be taken into consideration when preparing such a programme.



Expert Meeting on the Toxicity of uPVC pipes
and coagulant aids

The Hague, 8-12 February 1973

Proposed items for general discussion
of toxicity of uPVC pipes
agenda item 5.3

- 5.3/1 Discussion on the establishment of a toxicological
WHO expert committee on new waterworks
Chemicals (proposal Dr. Benes)
Proposal of expert group
- 5.3/2 Discussion of existing test methods for new uPVC drinking
water pipes
Proposals of expert group
- 5.3/3 Procedure for the establishment of
- test programme
- permitted levels
- approved analytical methods
Proposals of expert group
- 5.3/4 Toxicological review of leaching of toxic substances
from uPVC drinking water pipes
- 1) lead compound
 - lead levels in new PVC distribution systems
 - initial lead leaching from new uPVC drinking water pipes
 - permitted levels, proposals of expert group
 - 2) organo-tin compound
 - organo-tin levels in uPVC distribution systems
 - initial organo-tin and tin leaching
 - permitted levels, proposals of expert group
 - 3) cadmium
 - the advisability of cadmium for uPVC pipe production,
proposal of expert group
 - 4) other toxic substances
 - proposal of expert group
- 5.3/5 Further additional tests
Proposals of expert group

HEALTH ASPECTS RELATING TO THE USE OF
uPVC PIPES FOR COMMUNITY WATER SUPPLY

M. Fontana

Report of a Consultant Group

VI. 1.4

C O N T E N T S

1. Introduction
 2. Historical review of the use of uPVC pipe for drinking water supplies
 - a) Europe
 - b) U.S A.
 - c) Other countries
 3. Description of materials and production techniques
 4. Toxicology of uPVC and its additives
 - a) uPVC
 - b) Lead
 - c) Organo-tin
 - d) Cadmium
 - e) Others
 5. Leaching of toxic substances from uPVC pipe
 6. Standards and Specifications
 - a) Pipe
 - b) Water
 7. Test Methods
 - a) Pipe
 - b) Water
-

HEALTH ASPECTS RELATING TO THE USE OF
uPVC PIPES FOR COMMUNITY WATER SUPPLY

Report of a Consultant Group

A Consultant Group met in The Hague from 8 to 12 February 1973, convened by the WHO International Reference Centre for Community Water Supply (IRC) to review current practice in the use of uPVC pipe with specific reference to toxic substances which may leach out from the material of the pipe used for conveying drinking water. Mr. P. Santema, Director of the IRC opening the meeting, emphasized the importance of protecting drinking water quality in the context of increasing environmental contaminants, and drew special attention to the need for surveillance of possible health hazards of new water supply materials.

1. Introduction

uPVC pipes are widely used in the industrialized countries. However, it is in the developing countries where their increasing use is likely to have a substantial health impact through the provision of piped drinking water to the greatest number of people possible. uPVC pipes have the advantage of lower costs, ease of laying and corrosion resistance amongst others.

Over million people or roughly% of the total population of 90 developing countries were not serviced by safe piped water supply as of 1970.¹⁾ However, this very wide use of uPVC pipes has also brought to fore the question of toxicity arising out of the leaching of heavy metal stabilizers and associated impurities from the pipe-wall material into the water. The testing procedures and results from the WHO supported research projects undertaken by Water Research Association (WRA) in the United Kingdom and by the Testing and Research Institute of the Netherlands Waterundertakings : KIWA Ltd. in the Netherlands taken together have been at variance in some respects with those of the National Sanitation Foundation in the United States of America. As such it had become necessary to review the test procedures and analytical methods for extraction of stabilizer material from the pipe as well as experience on leaching of lead from lead-stabilized pipes from many countries as possible, and arrive at a consensus on methods, procedures and standards.

1) World Health Organization (1972) Doc. WHA 25/ Report of the Director-General to the Twenty-fifth World Health Assembly on Progress in Community Water Supply

2. Use of Unplasticized PVC Pipe for Drinking Water Supply

Historical Review

Europe

Although in 1912 PVC production on a technical scale was made possible in Germany by direct reaction of hydrochloric acid and acetylene using catalysts, PVC pipe could not be manufactured before 1935, when problems of head stabilisation and PVC quality were solved. In Germany the I.G. Farben Industrie installed on an experimental basis 400 drinkingwater installations by using PVC pipe between 1936 - 1939 (ref. 5). The first DIN specifications were completed in 1941. After world war II contacts between plastic manufacturers and waterworks organisations resulted in many experimental projects in which uPVC drinking water pipe have been used. Until the second half of the fifties many problems such as cold brittleness, installation technicalities, joints and fittings had to be solved. In the Netherlands the first draft test-specifications for uPVC drinking water pipe were completed in early 1954. This draft was approved in September 1956. The test specification included hygienic and toxicological demands concerning leaching of toxic materials from uPVC material. This part of the test specification was used as a model for setting up several European test specifications such as in England, Norway, Belgium, Italy and was also used by ISO, In 1955 the Technical Committee 5 of the ISO installed the Subcommittee 6 which started their activities on standardization of uPVC pipe.

The Subcommittee 6 has been transformed into Technical Committee 138 in September 1970.

Since the end of the fifties the water supply has been a big market in Europe for uPVC pipe particularly for water mains and service pipes. Table 1 illustrates the use of uPVC drinking water pipe in the Netherlands (mains and service pipes).

Table 1

uPVC drinking water pipe
in the Netherlands

Year	km installed
1962	2400
1963	2800
1964	3300
1965	3000
1966	2900
1967	2700
1968	2000
1969	2000
1970	1900
Total 1962-1970:	23000

For the United Kingdom, the use of uPVC water pipe continues to increase considerably as indicated by the collated sales figures for PVC pipe to BS 3505/3506 (unplasticized PVC pipe for cold water supply) given in table 2.

Year	1966	1967	1968	1969	1970
Sales of PVC pipe to BS 3505/3506 (tons)	9169	12710	15041	18810	30343

United States

Plastic pipe used for potable water applications in the U.S.A. is evaluated by the National Sanitation Foundation (NSF) to ensure conformance with NSF Standard 14 (). The purpose of this standard is to establish the necessary public health and safety requirements for thermoplastic materials, pipe, fittings, and joining materials based on specific use and application, including potable water, and to provide for conditions and provisions of evaluation thereof.

Development of Standard 14 was preceded by a three year study () undertaken at the request of the plastics industry, and mutually endorsed by leading health and water utility officials to determine the suitability of plastic pipe for use with potable water. Specific goals were to establish whether, a) any substances that might be deleterious to health would be extracted from the plastic by an aggressive potable water, and b) the passage of water through plastic might effect the appearance, odor, or taste of the water.

The study began in 1952 under the sponsorship of the Society of the Plastics Industry for its Thermoplastic Pipe Division and suppliers of plastic materials. An advisory committee representing industry, regulatory and user groups guided the study. Twenty-two samples of plastics most commonly used for conducting cold water as well as proposed new formulations and a few plastics not recommended for use with potable water, were subjected to hundreds of chemical, organoleptic, and toxicological tests. Tin stabilized PVC pipe was included in the 22 samples.

Basic extraction and testing procedures developed during the three-year supportive research program are utilized today in the continuing evaluation and listing program at NSF. Contents of the standard are reviewed at intervals of not more than

three years to maintain current and effective requirements consistent with advancing technology. Analytical methodology is similarly reviewed and updated to provide better instrumentation and internal quality control in the testing program.

All samples to be evaluated at NSF are collected by NSF personnel, from manufacturing plants, warehouses, or points of installation on a random basis, at unannounced visits and intervals. Permission to use the NSF seal on plastic pipe for potable water applications is contingent upon demonstrated compliance with Standard Number 14.

To date, more than 20,000 samples of plastic pipe have been evaluated.

According to the Plastics Pipe Institute the total plastic pipe Production in 1967 for water supply and distribution amounted to 123,000,000 pounds, being 36% of the total plastic pipe production by end use. PVC, PE and ABS, in that order, are the major plastics used for pressure pipe for potable water service.

Annual total plastic pipe production in the U.S. in 1972 was valued at \$350,000,000. meaning a doubling of the 1967 production within 5 years. Figure 1 illustrates the U.S. plastic pipe production from 1962 to 1967 (ref. 7)

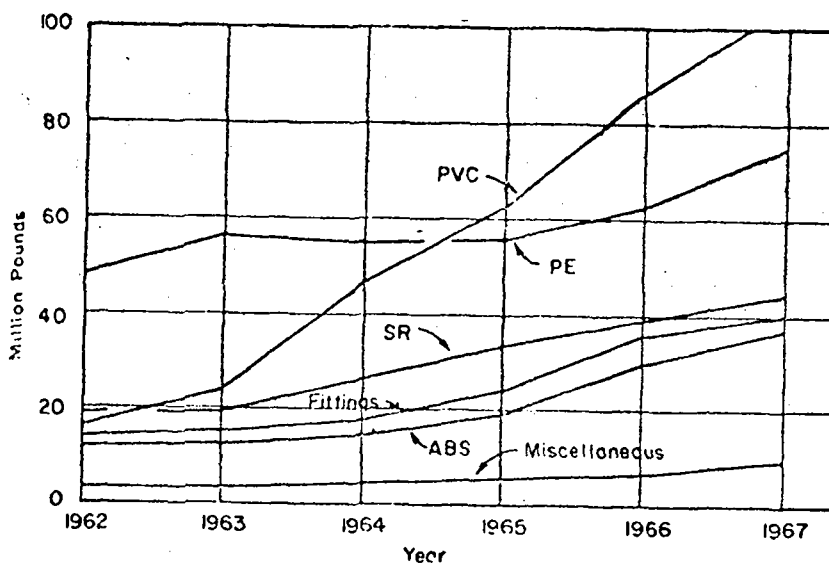


Figure 1

Other Countries

PLASTICS PIPE PRODUCTION BY MAJOR CATEGORIES

As the potential market for sale of uPVC pipe is limited by shipping costs, uPVC pipe is usually manufactured locally, for Latin America mostly by U.S. owned or affiliated manufacturers (ref. 7). In Asia some European owned manufacturers are operating. There is a large manufacturing capacity based in Japan.

3. Description of Materials and Production Techniques for uPVC Pipe

Two types of polymerized vinylchloride are used for uPVC pipe production, i.e. emulsion PVC and suspension PVC.

For uPVC drinking water pipe in England, Germany and the Netherlands suspension PVC has nearly always been used. The advantages of the latter type of PVC are a higher purity, larger particle size so that single screw extruders can be used, and less water uptake. The suspension PVC may still contain small quantities of polymerization catalysts such as inorganic mercury compounds, organic peroxides, Azo-compounds, persulfates and other products acting as redoxsystems, and water soluble suspension catalysts as organic colloids f.a. gelatin, pektin, polyacrylates, polymethacrylates, polyvinylalcohol and organic compounds as talcum, calcium phosphate and magnesiumphosphate.

uPVC pipe is made by extrusion of thermoplastic PVC using single or multiple screw extruders. Figure 2 illustrates a vented single screw extruder (ref.7).

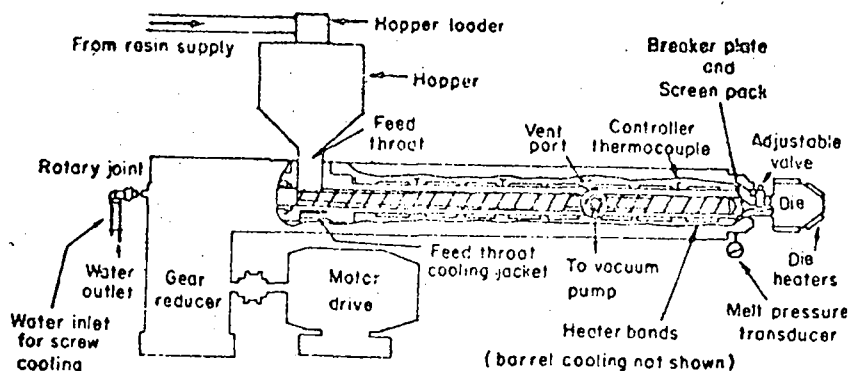


Figure 2
VENTED SINGLE SCREW EXTRUDER

Due to the high chloride content, PVC is unstable at temperatures exceeding 120°C. Because of thermoplastic deformation of the PVC temperatures between 150°C and 200°C are sufficient, heat stabilizers have to be added to the PVC material before entering the extruder. Besides heat stabilizers, lubricants are added to reduce internal and external friction during extrusion and light stabilizers and pigments are added to reduce PVC deterioration by UV radiation and to prevent growth of phytoplankton. Some manufacturers use PVC granulate already containing the required additions.

In most European countries toxic lead compounds as lead stearate, di basic lead

stearate, di basic lead sulfate are used as heat stabilizers and lubricants.

Di basic lead phosphate acts as light and heat stabilizer. Lead stabilizers are relatively insoluble in PVC. Non toxic compounds such as calcium stearate acts as a lubricant and as a weak heat stabilizer .

Lead compounds, sometimes in addition to products with synergistic action as barium + cadmium laurates, are used. Quite a substantial proportion of organo-tin stabilizers are used in fittings and pipe in the U.S. Barium-Cadmium compounds however are usually not allowed in food packing material but it is known that they are sometimes used for uPVC drinking water pipe produced outside of the U.S.

It is clear that the use of toxic stabilizers for uPVC drinking water pipe is permissible only when leaching of the toxic compounds is restricted to an insignificant level considering the toxicological effects of the water quality.

This includes:

a) The quantity of toxic stabilizers or reaction products of stabilizers and hydrochloric acid, as a degradation product of PVC produced during extrusion, present on the surface of the pipe must be as low as possible.

These compounds give rise to an initial high lead or cadmium concentration in the drinking water during the period directly after installation.

b) The toxic stabilizers must not be allowed to migrate to the surface area, for such migration will give rise to prolonged high levels of toxic materials in the drinking water.

In the U.S. no lead and cadmium compounds are used for uPVC drinking water pipe production. As a result, tetra valenced organic tin compounds were developed for heat and light stabilisation. These compounds are soluble in PVC. Although organo-tin compounds cannot be regarded as non toxic, they are assumed to less acute toxicity than lead because they have no cumulative effects. Less organo-tin is required for stabilization in uPVC pipe (0.3% Sn va. >1% Pb), thus now equal to or slightly lesser than that of lead (ref.)

In addition, tin stabilizer is not used as a lubricant, thus the tin does not form a metal-rich film on the inner surface of the pipe as is the case with lead stabilized pipe, where the stabilizer is used, in whole or part, as the lubricant.

4. Toxicology of uPVC and its additives

a) uPVC

in production

5. b) Lead

The Sixteenth Report of the Joint FAO/WHO Expert Committee on Food Additives 1972 (WHO Technical Report Series No. 505) evaluates available information on lead intake of man from environmental sources (air, water, food). Lead is a cumulative poison. Ingested lead of course depends on dietary factors such as content of calcium, phytic acid, proteins etc. Absorption from air depends partly on particle size. About 10% of lead in food and water, and as much as 40% from air, may be absorbed. Considering that lead is a cumulative poison, the Committee established in adults a provisional tolerable weekly intake of 3 mg of lead per person, equivalent to 0.05 mg/kg body weight per week. This level does not apply to infants and children who are a high risk group.

Meeting after the publication of WHO International Standards for Drinking Water 3rd Edition, was published in 1971 this joint FAO/WHO Expert Committee had this to say on the standard: "The levels of lead encountered in water supplies are probably about 0.01 mg/litre. However the International Standards for Drinking Water suggest a tentative limit for lead of 0.1 mg/litre. Assuming a consumption of 2.5 litres of water per day the maximum lead intake from this source would be 250 ug; this would contribute significantly to the total amount of lead taken in by man". On the basis of this review, it is quite possible that the maximum permissible level of lead in water may well be reduced to 0.05 mg/l in the fourth edition of the International Standards for Drinking Water

4. Toxicology of uPVC and its additives

c) Organo-tin

in production

5. d) Cadmium

The toxicity of Cadmium was evaluated recently in the sixteenth Report of the joint FAO/WHO Expert Committee on Food Additives 1972 (WHO Technical Report Series no. 505)

Absorption of Cadmium from air is insignificant. Preliminary results on total diet studies indicate daily intakes varying according to country, from 50 to 150 micrograms per day.

Municipal waters in industrialized countries generally contain less than 1 microgram of Cadmium per litre. The tentative upper limit set in the International Standards for Drinking Water (1971) is 10 micrograms/litre.

On the basis of an estimated daily consumption of 2.5 litres, this would amount to a maximum Cadmium intake of 25 micrograms per day. There may also be some cadmium dissolution from galvanized pipes. Elevated levels occur in foods, particularly in crustacea and shellfish, in association with zinc levels, and the levels are even higher if there is contamination of the estuaries with cadmium. Likewise cadmium can enter food from contaminated food used to irrigate crops.

Cadmium is apparently a nonessential trace metal that is virtually absent at birth and accumulates with age reaching to a maximum of about 25 to 30 mg in a person occupationally non-exposed. It has also a high demonstrated toxicity. The target organ for ingested cadmium is the kidney. Renal damage level is estimated at 200 mg/kg body weight. Environmental contamination of food and water by cadmium has been implicated as the cause "itai-itai" disease in Japan. Levels of cadmium in renal cortex of person occupationally non-exposed varies from 30 mg/kg in Sweden, 25-50 mg/kg in U.S.A. to 50-100 mg/kg wet weight in Japan. In view of the closeness of these levels to the critical level of 200 mg/kg, the joint FAO/WHO Expert Committee felt that present day levels of Cadmium in the kidney should not be allowed to rise further, and recommended that every effort should be made to limit and even to reduce the existing pollution of the environment with cadmium.

4. Toxicology of uPVC and its additives

e) Others

in production

5. Leaching of Toxic Substances

All standards and specifications include a general demand on the composition of the material such as "The material shall contain no ingredients in an amount which has been demonstrated to migrate into water in quantities which are considered toxic. The water which has been in contact with the plastic material must meet or exceed official quality standards". Additions may only be utilized when required to realize the polymerisation process and to make possible the extrusion of uPVC pipe. Innocuous tracers to materials may be used in so far the specifications can be met.

There is an evidence that pipes complying with the standards relating to the use of lead stabilizers in uPVC will not produce concentrations of lead in drinking water in excess of the upper limit of concentration established by WHO (0.1 mg/l).

- In 1959, Boelens (ref. 16) examined water samples from 24 uPVC mains in the supply area of the Waterworks Overijssel before and after a period of standing of the water in the pipe, ranging from a few hours to 9 months. The period that the pipe had been in service ranged from 2 months to 5.5 years. Sixty tests have been made and only two samples contained a lead concentration greater than 0.05 mg/l after a period of standing that lasted 4 months and some days. The lead concentrations respectively amounted to 0.07 mg/l and 0.10 mg/l. The nominal diameters of the pipes ranged from 15 - 100 mm.

- In 1961 the "Bundesgesundheitsamt Berlin" carried out a similar survey in some other parts of the supply area of the same waterwork (ref. 17). Water samples have been taken from ten uPVC mains before and after a period of standing. Out of 20 samples the lead content of one sample passed 0.05 mg/l after a standing period. The lead concentration amounted to 0.09 mg/l after a standing period of 12 hours.

- The KIWA Committee on Plastic Water Pipes took water samples from 11 uPVC water mains at three different times after standing periods from 12-24 hours (ref.18). The mains were located in various places throughout the Netherlands. From 33 water samples, 14 proved to have lead contents which exceeded 0.05 mg/l after periods of standing. None of the samples exceeded the Dutch standard of 0.3 mg/l of lead after standing for 16 hours (ref.19)

- Everard reports experiments in which hard water was allowed to stand in uPVC pipes manufactured to B.S, 3505 for periods ranging from 22 hours to 28 weeks (ref. 20). The lead contents of the water after these periods of standing was reported as 0.1 mg/l in nearly all cases.
- Visintin and Monteriolo (ref. 21) examined water samples from Italian uPVC mains of length varying from 250 m to 4 km. The lead contents of the uPVC from which these pipes were made varied between 0.031 - 1.619% and the pipes had been in service for periods ranging from a few weeks to three years. It was found that the concentration of lead was less than 0.07 mg/l in 31 out of 32 pipes. A concentration as high as 0.09 mg/l was found only in a new 4 km main. After three years service the lead content of the water in the same pipe was at the extent of 0.01 mg/l.
- Cosoveanu (ref. 22) carried out series of tests on uPVC pipe of Rumanian manufacture and showed too that the quantity of lead, extracted by water from a new pipe, decreased rapidly.
- Tests conducted in Peru (Bracale, Chuy) in 1967 lead to these conclusions (Private communication):
 1. The concentration of lead in the extracting water is extremely low for PVC pipe stabilized with lead and is much lower than is permitted by the standards for potable water.
 2. The quantity of lead decreases in time, after being proved experimentally in the laboratory and by analysis of samples, taken from the distribution systems so that the total amount of the extractable lead is depleted in a no greater period than 90 days.
 3. It is considered that these pipes under normal service conditions offer no risk for the health of the users of potable water systems. (Peru specifies that only calcium and zinc may be used as stabilizers for drinking water pipes).
- Paramasivam, et al. evaluated uPVC pipe samples from four Indian manufacturers (ref.-) Tap water was allowed to flow through new pipes 4 m long at a velocity of 4 m per minute. One sample fully complied with the current ISO draft standard. In the other three samples, lead levels in the first extract exceeded the ISO maximum permissible level (1.0 mg/l), however levels in the third extract were within the ISO limit (0.3 mg/l).
- (Details of the Bulgarian study will be added if available)

- WRA studied water mains ≥ 25 mm nominal bore in service in the United Kingdom. The pipes were made in accordance with BS 3503. The sampling programme was designed to cover as many different situations as possible. Distribution systems were therefore surveyed to supply water, covering a range of compositions. Samples from old and new pipes of various sizes and manufacturers were obtained from where ever possible. Many pipes were sampled under both normal and high flow conditions. Of 77 samples examined 37 were found to have a lead concentration 0.01 mg/l or less and none exceeded 0.05 mg/l. In addition to the general survey a newly installed pipe was sampled during a period of 32 days to determine the trend of lead levels.

Table 3 gives the results.

Table 3 lead concentration in water from a new 25 mm nominal bore uPVC service pipe.

Length of pipe prior to sampling point 6.1 m. Manufacturer S. Water Analysis 0.

Period in service days	Total volume of water passed m ³	Static sample		Flowing sample. Lead content mg/l
		Standing period hours	Lead content mg/l	
0	0	14	0.11	0.01
1	0.83	14	0.03	0.06
4	1.64	62	0.09	0.02
5	2.46	14	0.02	0.02
6	3.26	14	0.01	0.02
7	4.10	14	0.02	0.01
8	4.91	14	0.01	0.01
11	5.74	62	0.02	0.01
12	6.54	14	0.06	0.01
13	7.38	14	0.02	0.01
14	8.30	14	0.02	0.02
15	9.00	14	0.02	0.01
18	9.85	62	0.02	0.01
29	17.2	14	0.01	0.02
32	18.2	62	0.01	—

Recently the WRA investigated the loss of extractable lead (using the nitric/perchloric acid extraction method) with time when a new 32mm nominal bore uPVC pipe had water passed through it continuously at a rate of 0.2 litre/sec. The results are given in Table 4.

TABLE 4

Period of flushing (days)	0	3	9	27	81
Extractable lead mg/m ²	28.3	9.4	5.2	3.5	2.7
% removal of extractable lead	-	67	82	88	91

A high proportion of the extractable lead was removed in the first 9 days flushing but further removal was slow.

In another series of tests a large batch of uPVC pipe was extracted 5 times with nitric/perchloric acid mixture and then reextracted after periods of storage of between 3 and 243 days. Half of the pipes were stored empty while the others were stored full of water. In all cases a small 'recovery' of extractable lead was found (usually less than 1mg/m²) but there was no evidence that this increased with period of storage. The 'recovery' of extractable lead tended to be rather less with pipes stored full of water.

- In 1969 water samples were collected from water mains and connected uPVC service pipes in the Netherlands. Pipe was made in accordance with nr. 49. The water quality concerned includes the greatest possible differences occurring in the Netherlands. In total 11 of the 18 mains were made of uPVC, 4 asbestos cement and 3 cast iron. In 9 of the 18 water samples no lead could be detected (less than 0.001 mg/l), in one uPVC water main the lead level increased 0.05 mg/l (0.055 mg/l) as laid down by the former WHO International Standards.

The water appeared to be contaminated with ferric hydroxide flakes so that adsorption of lead may have been occurred. Water samples taken from a connected uPVC water pipe did not contain any measurable lead in normal flowing conditions.

Flowing samples were taken from 22 uPVC service pipes. The lengths varied from 4 to 452 meters, the oldest pipe was laid in September 1955, the newest had only been in service for 1 month. The nominal bore varied from 16 to 50 mm. Lead levels appeared to be < 0.01 mg/l.

In total 25 uPVC service pipes were sampled after periods of standing which ranged from 10 minutes to 114 days. For 10 of the 25 samples, the lead concentration in the water at the end of the standing period amounted to < 0.001 mg/l; for 8 samples 0.01 mg/l; for one sample 0.015 mg/l, for one

sample 0.03 mg/l, for one sample 0.04 mg/l and for one sample the exceptionally high value of 0.6 mg/l.

The standing period in the last uPVC pipe amounted to 84 days. After flushing the uPVC pipe with a quantity of water equal to two times the content the lead concentration amounted to 0.01 mg/l.

~~Besides~~ ^{IN ADDITION TO} the field survey the initial lead leaching ^{from} of 8 different uPVC pipes of 4 different makes were studied using drinking water of the Hague. The nominal bores amounted to 16 and 25 mm. Graphs one and two give the results. It can be seen that the main lead leaching during flow is restricted to the first 30 minutes and that the highest lead concentrations occur in the pipes with the smallest diameter.

~~From the work of KIWA can be concluded that with exception of one high value of 0.6 mg/l, the average increase of the lead concentration in the drinking water after standing periods in uPVC pipes is 0.004 mg/l. Under conditions of flow, the average decrease in the lead content in the water is 0.001 mg/l.~~

^{IN THE KIWA STUDIES,}
~~From the work of KIWA can be concluded that with exception of one high value of 0.6 mg/l, the average increase of the lead concentration in the drinking water after standing periods in uPVC pipes is 0.004 mg/l. Under conditions of flow, the average decrease in the lead content in the water is 0.001 mg/l.~~

- In the U.S. lead levels even measured in a series of extraction on three samples of uPVC pipe. One sample was pipe made in the U.S. from DWV application, and two were fabricated to conform with BS 3503. Lead levels exceeded established WHO maximum permissible limits in each of the first three extractions made on the U.S. made sample. In one of the British samples lead in the first extraction exceeded the WHO limit but the third extraction conformed. All extractions made on the second British sample contained acceptable lead levels (WHO limits).

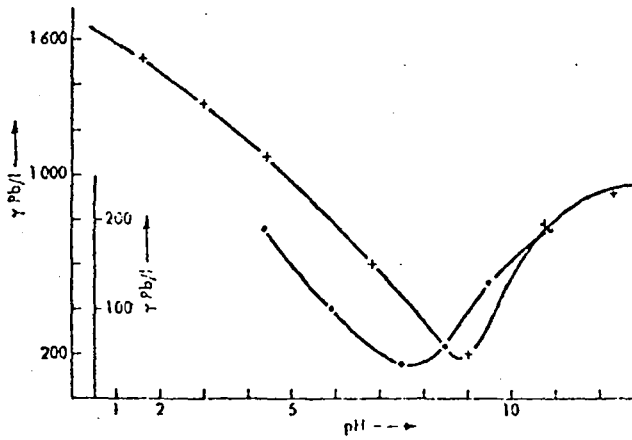
Quality characteristics which affect lead levels in uPVC drinking water pipe

As drinking water normally has been treated in Europe no big changes in water quality may be expected. In practice lead leaching from uPVC pipe appears to be very low and no effect of the water quality on lead levels could be determined.

Effect of ^{pH} acidity and temperature

Sontheimer and Wagner (ref. 23) studied the effect of acidity temperature and sodiumchloride on lead leaching from new uPVC pipes. Graphs 3 and 4 show the effects of pH and temperature.

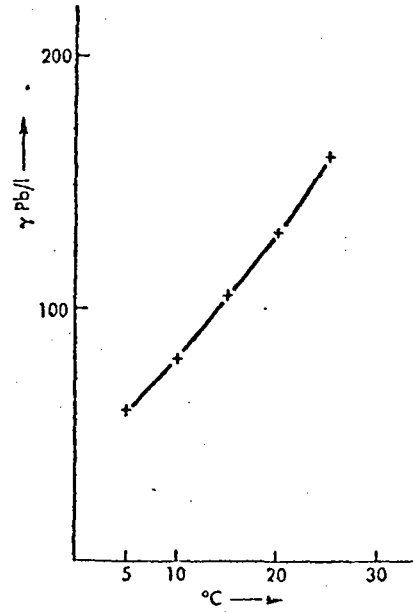
Graph 3



The effect of pH on lead leaching, standing period: 24 hours

- x— without pre-treatment
- after 5 extractions with 0.01 M NaHCO₃

Graph 4



The effect of temperature on lead leaching, standing period: 24 hours
(extractant: 0.01 M NaHCO₃)

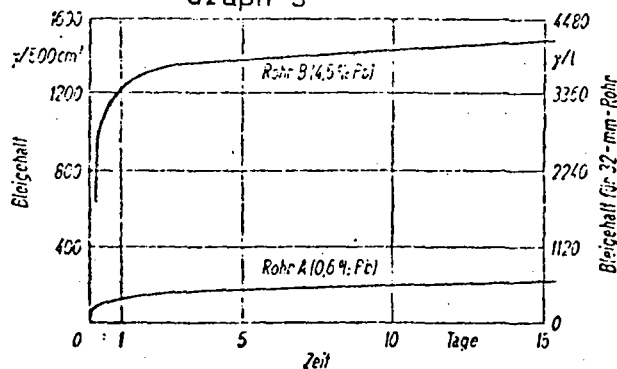
Effect of sodium chloride

Sodiumchloride did not effect the lead leaching between 5 and 100 m Mol/l.

Effect of lead content in uPVC

Niklas and Meijer (ref. 24) studied the effect of the lead content of new uPVC material on lead levels in drinking water. Standing periods lasted 15 days at a temperature of 20°C. Graph 5 gives the results. It can be concluded that lead levels were about seven times higher using uPVC pipe with 4,5 % lead in weight in comparison with a pipe containing 0,6% lead.

Graph 5



Effect of polyphosphates

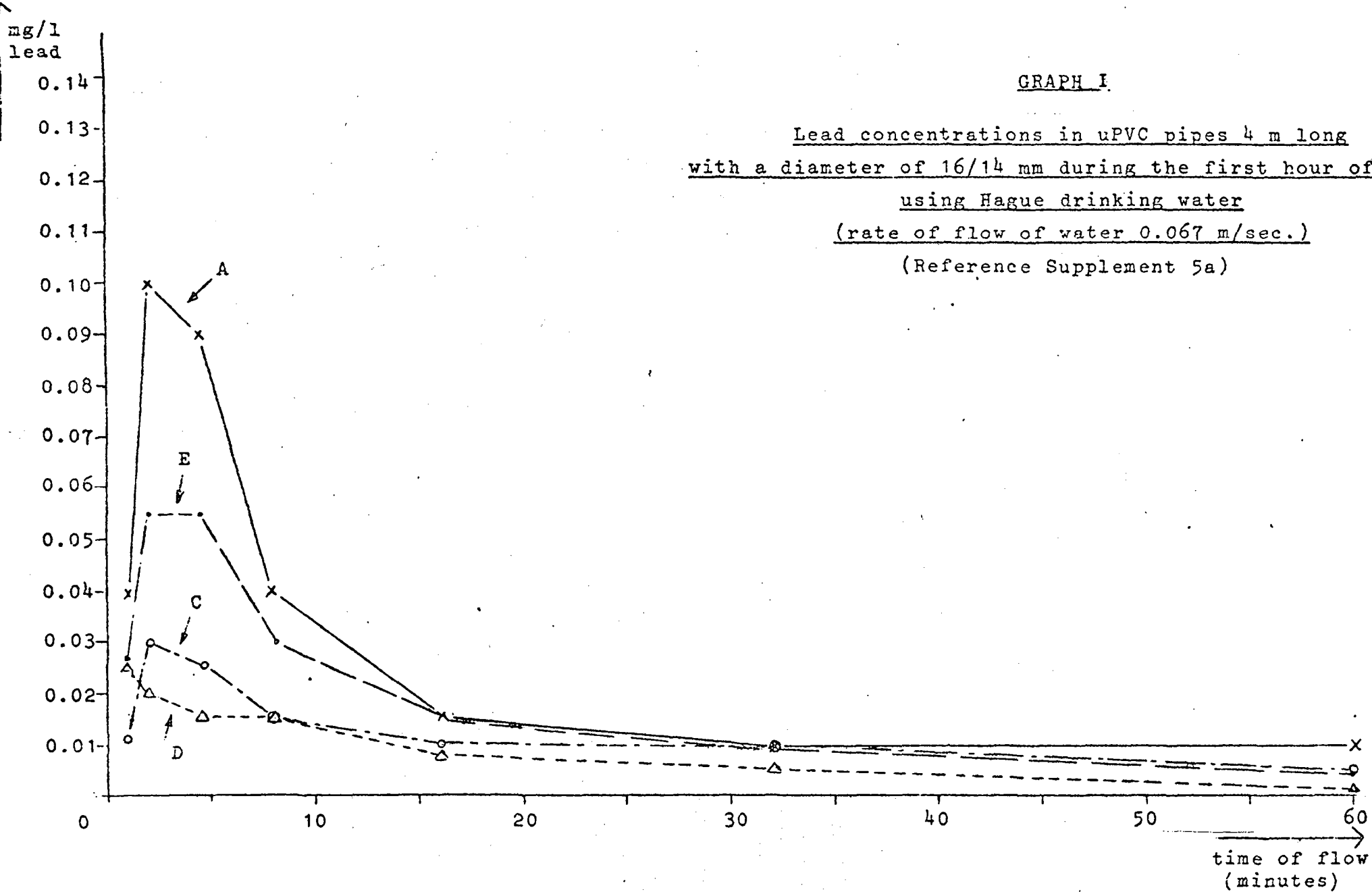
The effect of sodiumhexametaphosphate on the extraction of lead from uPVC pipe was investigated by the WRA. It was found that the presence of 5 mg/l of sodiumhexametaphosphate more than doubled the amount of lead extracted initially from new pipe with water. On a sample of pipe that had been in service for 9 months the effect was very small of negligible.

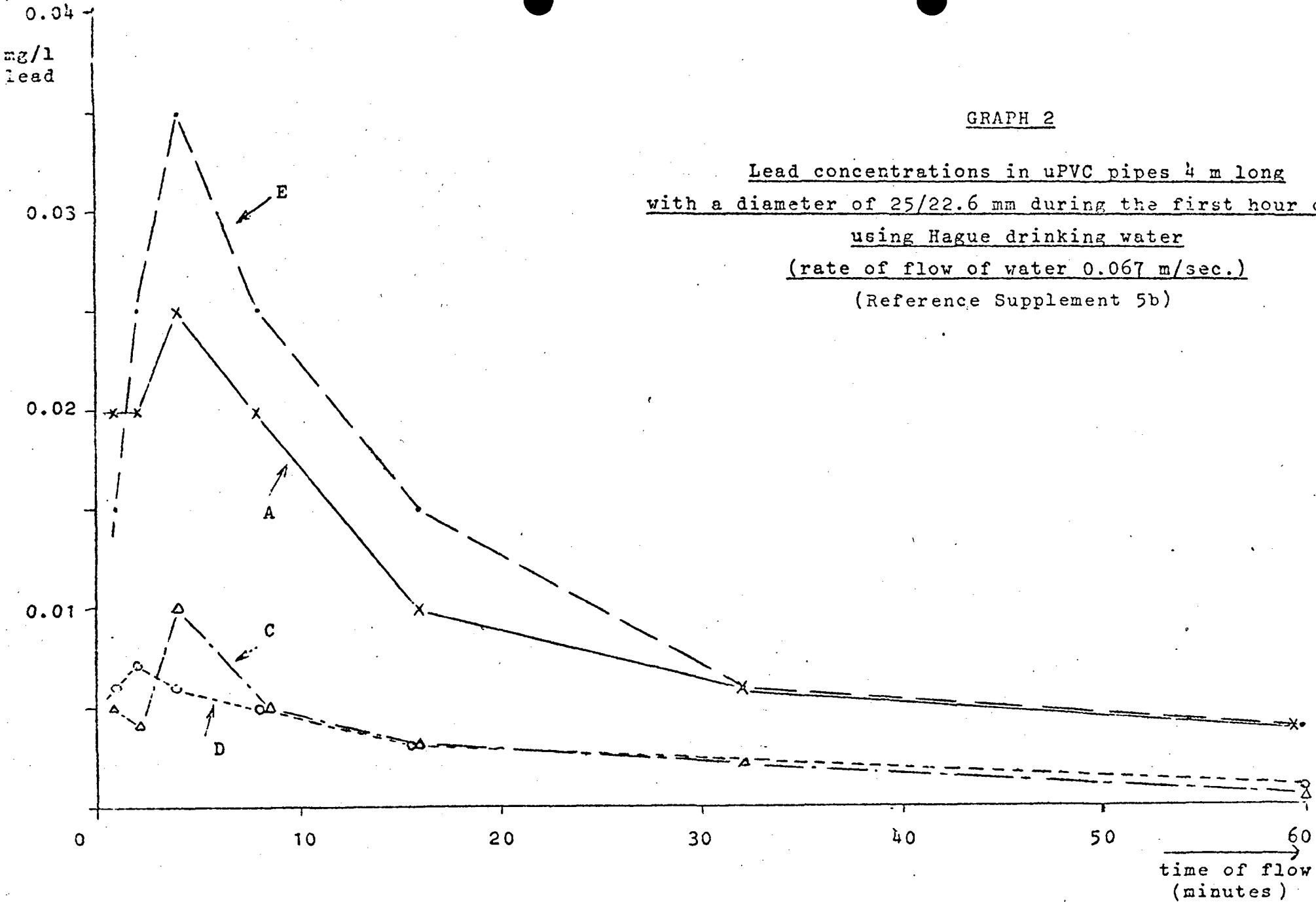
Test for extractable lead

The results of the survey of lead concentrations in uPVC distribution systems have proved that the existing tests based on the I.S.O. type have reassured that no long term health hazard due to the use of lead stabilizers in pipes meeting the standards was indicated. The potential hazard was essentially short term in nature and could not realistically be assessed in relation to the WHO standards for drinking water in which the levels, set for toxic substances, were based on exposure to the toxic substance during a lifetime. According to Packham of the WRA a test of shorter duration, with a stable extractant and involving a degree of agitation would have advantages especially in terms of convenience over the procedures of the ISO type (ref. 1 and 3). Packham states that it is questionable, however, whether an arbitrary test is a satisfactory basis for a standard. The test as it stands provides a measure of the level of extraction at some indefinite time in the life of a pipe.

GRAPH I.

Lead concentrations in uPVC pipes 4 m long
with a diameter of 16/14 mm during the first hour of flow
using Hague drinking water
(rate of flow of water 0.067 m/sec.)
(Reference Supplement 5a)





Since stabilizers may be leached of uPVC at different rates depending on the nature of the stabilizer and the way of how the uPVC is processed, the test provides no indication of either the initial or the ultimate rates of leaching. The above mentioned test is based on the widely held belief that all the extractable lead stabilizers contain a lead rich layer larger at the surface of the pipe.

After having tested several extractants, a 0.5% nitric acid - 0.85% perchloric acid - was selected as extractant, because this extractant effectively leached lead compounds without effecting the uPVC material. From the investigations of Packham appeared that the time of agitation is less important than the number of extractions. The procedure proposed to include six extractions, each of 60 minutes.

The KIWA compared the testing procedures for lead leaching according to the I.S.O. method and the WRA. The "total" lead leaching according to the WRA method was compared with the "total" lead leaching according to the I.S.O. method and the lead concentrations during flow tests, using drinking water of the Hague (ref. 4). Table 4 gives the results. In so far the "total" lead leaching is concerned it was concluded that neither the WRA method nor the I.S.O. method correlate with the initial lead levels which appear after the first periods of standing directly after the installation of new uPVC pipe. As the lead concentrations are effected by the pH of the extractant and the lowest lead levels are to be expected at pH 7 - 8, the lead concentrations in the I.S.O. extracts (pH 4.6) are commonly higher in comparison with the lead levels after periods of standing using drinking water with a pH of about 7 - 8. It is to be expected in practice that the differences between the lead levels of the first and second extracts are in some way indicating the decrease in lead levels after successive periods of standing. Concerning the lead levels of the extracts, the I.S.O. method indeed simulates an "agressive" type of drinking water.

As to the uPVC pipes which are included in the investigations of the KIWA (four different makes, three different diameters each) the "total" lead leaching calculated from the I.S.O. extracts (pre-flushing during 1 hour) amounted to 16 - 87% of that determined according to the WRA method using successive extractions for 1 x 1 hour and 3 x 1/2 hours. An almost similar comparison made by the WRA in four different makes of PVC pipe resulted in a recovery of 30 - 64%.

In order to determine the influence of the duration of the pre-flushing period on lead leaching according to the I.S.O. method (pre-washing during 1 - 6 hours) the integrated lead leaching during the first, the first 2, the first 4 and the first 8 hours of pre-washing with Hague drinking water has been determined for 8 different uPVC pipe of 4 different makes. The values are given in table 4 . It can be concluded that a considerable

quantity of lead has leached during the pre-flushing and that the effect is the greatest for pipes with the smallest diameter. The result of the test according to the I.S.O. is strongly effected by the period of pre-flushing.

Table 4

The WRA flushed samples of 25 mm bore uPVC pipe for periods up to eight hours, then they are extracted for six hours with 150 mg/l carbon dioxide solutions. The experiments were repeated by using acetic acid sodium acetate buffer and sodium bicarbonate solution as an extractant. Table 5 gives the lead concentrations of six hour extracts.

Table 5 The effect of flushing time on the extraction of lead from uPVC pipes

Flushing time (hours)	Mean lead content (mg/l) of 6-hour extract using		
	CO ₂	CH ₃ CO ₂ H/CH ₃ CO ₂ Na	NaHCO ₃
0	1.62	0.59	0.28
½	0.23	0.31	0.15
1	0.17	0.16	0.07
2	0.13	0.25	0.07
4	0.11	0.21	0.06
8	0.11	0.18	0.05
8 (static)	0.55	0.62	0.13

Table 4 - Correlation between flow tests and extraction tests

1	2	3	4	5	6	7	8	9	10	11	12	13	14
		Lead leaching mg/100 cm ²						Lead concentration mg/l					
Manu- fac- turer	Dia- meter	WRA	ISO [#]	Hague water 10 x ext. 5 min. each	flow test Hague water		lead film deter- mined from bore tests	ISO		flow tests with Hague water			
					0-1 hour	0-24 hours		1st ext.	3rd ext.	max. du- ring flow 0-4 min.	after 16 min. of flow	after 24 hours flow and 48 hours standing	idem 5 min. flow and 72 hours standing
E	16/14	0.47	0.28		0.03	0.08	0.11	6.3	0.60	0.06	0.02	0.55	0.15
	25/22.6	0.41	0.30	0.05	0.04	0.18		4.2	0.53	0.04	0.02	0.32	0.23
C	16/14	0.25	0.20		0.02	0.14	0.14	4.9	0.45	0.03	0.01	1.00	0.32
	25/22.6	0.24	0.20	0.05	0.01	0.01		2.8	0.48	0.01	0.003	0.14	0.05
A	16/14	0.24	0.17		0.04	0.24	0.14	3.9	0.27	0.10	0.02	0.65	0.28
	25/22.6	0.20	0.11	0.06	0.03	0.04		1.0	0.43	0.03	0.01	0.41	0.33
D	16/14	0.14	0.02		0.01	0.02	0.14	0.13	0.16	0.03	0.009	1.05	0.85 ⁺
	25/22.6	0.09	0.03	0.02	0.01	0.03		0.16	0.17	0.007	0.003	0.16	0.36 ⁺

[#] 1 hour pre-washing

⁺ duplicate pipe after 5 min. flow and another 48 hours standing 0.06 mg/l

The results in table 5 show that the extraction levels decreased with increasing periods of flushing although the absolute levels of extraction differed according to the used extractant. In all cases the tendency of the results obtained after periods of flushing to level out for longer than one hour. Included in table 5 are the results of an experiment in which new pipe samples were filled with tapwater and allowed to stand for eight hours prior to extraction. The extraction levels in this experiment were three to four times greater than those which were obtained after flushing the pipes with tap water for the same period.

6. Standards and specifications

Usually the test specifications include a general demand by which the PVC pipe is not allowed to contain ingredients in an amount which has been demonstrated to pollute the water in concentrations considered toxic. In contrast with plastic wrappings for food and foodproducts uPVC drinking-water-pipe is used for a long time and contact with chemicals is limited to drinkingwater. For uPVC waterpipe this includes that both the initial and the long term leaching of toxic substances into the water must be taken into consideration and that the toxicological consequences of leaching of toxic substances restricted to a short period direct after installation cannot be considered in an equal way as for wrappings. In Europe test specifications of uPVC drinkingwater-pipe include toxicologic and ^{Sometimes} usually organoleptic demands. Toxicologic tests are mostly restricted to the leaching of toxic heavy metals using three successive extraction tests simulating the worst circumstances which may be expected in practice.

Maximum acceptable concentrations in the third extract should mostly be in accordance with approved maximum allowable concentrations of toxic substances in drinkingwater.

Most of the toxic heavy metals containing stabilizers used for stabilization of PVC may solve into the water to a certain extent and the uPVC material may very well contain up to 2% in weight.

No specific tests are related to other non metallic organic additions which may be present in small quantities.

In the United States the National Sanitation Foundation published their Standard No. 14 for Thermoplastic materials, Pipes, Fittings, Taps and Joining materials. Its purpose is to establish the necessary public health and safety requirements for the above mentioned thermoplastic materials.

The differences among test specifications and demands especially between Europe and the U.S. have resulted in a different point of view concerning the acceptability of lead stabilizers for uPVC drinking water pipes.

Studies by NSF have shown that lead leaching from new uPVC pipes gives rise to lead levels in extractant water which are not in accordance with the Public Health Service Drinking Water Standards - 1962 (PHS Publication no. 956) (0.05 mg/l) The point of view in several European countries is that lead leaching from uPVC is only significant a short period directly after installation and the lead leaching decreases rapidly to insignificant low amounts.

Most of the European test specifications concerning leaching of toxic heavy metals are based on that philosophy

Lead stabilized uPVC pipe of good quality can meet most European Standards but cannot meet the NSF Standards (see page .) In the present situation lead stabilizers are used in Europe and organo-tin stabilizers in the U.S.

Standards applied in different countries on uPVC drinking water pipe are mentioned below:

ISO Draft International Standards

ISO/DIS and

United Kingdom	BS 3505
Federal Republic of Germany/	DIN 8061 DVGW Arbeitsblatt 320 Mitteilungen XIX aus dem Bundesgesundheitsamt.
The Netherlands	KIWA Kwaliteitseisen no. 49
France	NF T 54-003 (July 1972) - Matières Plastiques - Tubes en polychlorure de vinyle non plastifié - Spécifications Générales. NF T 54-016 (July 1972) - Matières en Plastiques - Tubes en polychlorure de vinyle non plastifié pour la conduite et la distribution de l'eau avec pression - Specifications. NF T 54-017 (July 1972) - Matières Plastiques - Tubes en polychlorure de vinyle non plastifié pour installations sanitaires - Spécifications. NF T 54-019 (May 1969) - Matières Plastiques - Tubes en polychlorure de vinyle non plastifié pour la conduite de liquides alimentaires - Spécifications.
U.S.A.	National Sanitation Foundation Standard no. 14 NSF Publication "A study of plastic pipe for potable water supply"
Norway	Standard N 926
Poland	Standard PN - 65/C-89204
Ireland	IS 123
Australia	Standard ASK138 - 1969
India	Standard IS 4985 - 1968
Israel	Standard SI 532
South Africa	Standard SABS 966-1969

Test methods for toxicological and organoleptic properties of uPVC drinking water pipe
Table gives a survey of the test methods and maximum permissible levels as stated in the Standards Specifications.

2 pages to follow

Procedure specified	Pre-treatment	Extractant	Extraction period	max lead permitted	Additional requirements max. permitted
ISO Draft International Standard	1 - 6 hours pre-washing with water at 3m/min velocity. Rinse with distilled water.	150 mg/litre carbon dioxide in distilled water. Temp. $20 \pm 5^{\circ}\text{C}$	1. 48 hours 2. 48 hours 3. 48 hours	1.0 mg/litre - 0.3 mg/litre	
United Kingdom Australia India	6 hours pre-washing with tap water at 3m/min velocity. Rinse with distilled water	150 mg/litre carbon dioxide in distilled water. Room temperature.	1. 48 hours 2. 48 hours 3. 48 hours	1.0 mg/litre - 0.3 mg/litre	
Germany	1 hour pre-washing with tap water at 3m/min velocity	Sodium bicarbonate 0.01 N Temp.	1. 72 hours 2. 72 hours 3. 72 hours	under consideration	
The Netherlands	1 hour pre-washing with tap water at 3m/min velocity. Rinse with distilled water.	150 mg/litre carbon dioxide in distilled water. Room temperature.	1. 48 hours 2. 48 hours 3. 48 hours	1.0 mg/litre 1.0 mg/litre 0.3 mg/litre	
Ireland	1. Pushing a plug of cotton wool dampened with distilled water 2. 1-minute pre-washing with distilled water	0.01 m / 0.01 m acetic acid / sodium acetate buffer in distilled water. Room temp.	1. 48 hours 2. 48 hours 3. 48 hours	1.5 mg/m ² - 4.5 mg/m ²	
Poland	1. Pushing a plug of cotton wool 2. 1-hour pre-washing with tap water at 10 ± 2 m/min.	100 mg/l carbon dioxide in water. Room temperature.	1. 48 hours 2. 48 hours 3. 48 hours	1.0 mg/l - 0.1 mg/l	
U.S.A. (National Sanitation Foundation)	No pre-treatment	Carbon dioxide in Ann Arbor water pH 5.0 Temp. 100°F.	72 hours	0.05 mg/l	
Israel	1 minute pre-washing with ... water at m/min velocity	150 mg/litre carbon dioxide in distilled water. Room temperature.	1. 48 hours 2. 48 hours 3. 48 hours	1.0 mg/l 1.0 mg/l .03 mg/l	

7. Sampling Procedures

United Kingdom.

The PVC pipes to be tested are grouped according to their method of manufacture and the type of extrusion compound used.

Test specimens shall be taken at least once a year from the smallest size of pipe within each group. A change in the method of manufacture or in the extrusion compound leads to the establishment of a new group, test specimens will be taken from the smallest size of pipe within the new group.

Federal Republic of Germany

The frequency of testing must be at least once a year. In case of a change in the extrusion compound lead to renewed testing, the nominal size of pipe should at least be 40 mm.

The Netherlands

With the exception of a minimum age of the PVC pipe of 15 hours no specific demands have been prescribed.

France

NF T54-003 item 5 includes general descriptions.

U.S.A.

Policy B of the NSF Standard includes a statement of policy relating to sample collection - testing - reporting - samples required.

Item 1: "Actual laboratory examination of specimens of materials offered for use in the extrusion of plastic pipe is required and actual laboratory examination of specimens of extruded plastic pipe also is required before the right to use the NSF Seal of Approval on such materials and pipe is initially granted and at least once a year thereafter."

Item 2: "Actual laboratory examination of specimens of materials offered for use in the extrusion of plastic pipe is required and actual laboratory examination of specimens of extruded plastic pipe also is required before the right to use NSF Seal of Approval on such material and pipe is initially granted, and at least once a year thereafter."

South Africa

Sampling takes place according to a statistical procedure. Each sample of pipe should have a length of at least 12 meters. From each pipe 16 samples have to be prepared for extraction.

Australia

Three test specimens shall be taken from different pipes selected at random. To represent the batch a number of pipes are selected in a statistical way.

Marking

United Kingdom

"All pipes shall be indelibly marked at intervals no greater than 3 m. The marking shall show the following in the order stated:

- (1) The manufacture's identification
- (2) The number of this British Standard i.e. BS 3505
- (3) The nominal size, as shown in Table 1, and class.

Adhesive labels alone shall not suffice.

The marking shall be imprinted longitudinally in the following colours in accordance with BS 4159

Class B, red	Class D; green
Class C, blue	Class E, brown

It is strongly recommended that use is made of the same operated by the British Standard Institution where by the product may bear the registered mark of the BSI.

Federal Republic of Germany

DVGW Arbeitsblatt W 320: "The pipes have to be marked at distances of about 1 meter with DIN mark, name of manufacturer, number of extruder, code number concerning the composition of material, diameter and maximum working pressure.

The Netherlands

Chapter 2.10: "The pipes have to be continuously marked with name of manufactures of trade name (marque déposée) - KIWA - PVC - pressure class - nominal diameter x wall thickness (in mm) - production period - number of extruder, the last two dates may be in code.

France

According to NF T54-003 item 2.2 the next date must be marked on the pipe

- the name of the manufacturer
- the nature of the material of the pipe i.e. PVC
- the dimensions of the pipe

The colour must be:

- dark grey for drinking water pipe
- light grey for non-drinking water pipe

United States of America

An NSF Seal of Approval is applied on uPVC pipe meeting the NSF standard number 14. The material is "listed" by the NSF.

Section 4 - Requirements for pipe, fittings, valves and traps - item 4.03: Marking and coding of pipe, fittings and traps, and appurtenances:

"The manufacturer shall place on all thermoplastic pipe, fittings, valves and traps, and appurtenances, the designations and identification required in the latest applicable ANSI, ASTM or CS Standard(s) as determined by the NSF Joint Committee on Plastics. Provided, however that fittings and valves of such size and/or configuration as to preclude use of the complete marking shall be at least identified as to the manufacturer and type of material."

4.031 "All required markings shall be legible and so applied as to remain legible under normal handling and installation practices."

4.032 Thermoplastic pipe, in addition to the above, shall bear an appropriate code which will assure identification on the pipe as to the month of production and resin formulas used in the production of said pipe.

Manufacturer shall maintain such additional records as are necessary to confirm identification of all pipe so coded.

Australia

All pipes shall be indelibly marked at intervals of not more than 3 ft using a distinctive colour. The following information shall be shown:

- the name of the manufacturer and or the trade mark
- the nominal size
- class of the pipe
- suitable for potable water
- number of the standard

South Africa

Information shall appear in legible and durable marking of each pipe at intervals of length not exceeding 1 m:

- the name of the manufacturer of trade mark of the product or both
- nominal size
- class of the pipe
- identification of the batch

Requirements to the PVC pipe material

United Kingdom

The material from which the pipe is produced shall consist substantially of polymylchloride, to which may be added only those additives that are needed to facilitate the manufacture of the polymer and the production of sound, durable pipe of good surface finish, mechanical strength and opacity. Non of these additives shall be used seperately or together in quantities sufficient to constitute a toxic hazard, or to impair the fabrication of welding properties of the pipe or to impair its chemical and physical properties as defined in the standard.

Federal Republic of Germany

DIN 8061 chapter 2.1: "Modified PVC without plasticizers have to be used. The choice of stabilizers etc. are due to the manufacturers with the restriction that uPVC pipe has to meet the DVGW Arbeitsblatt and the quality demands of the Bundesgesundheitsamt."

DVGW Arbeitsblatt W 320: "Products of unknown composition and rework material are not allowed to be used."

According to th 11. Mitteilung aus dem Bundesgesundheitsamt uPVC drinking-water pipe is safe for conveyance of drinkingwater in case the material meets the prescribed composition.

Two-basic lead-stearate; two basic lead sulfate, two basic lead sulfite and two basic lead phosphite may be used totalling till 2 % in weight for lead as a maximum.

The Netherlands

"The material from which the pipe is produced shall consist on unplasticized polyvinylchloride to which may be added only those additives which are needed to facilitate the manufacturer of the polymer, and the production of the pipe. Pigments may be added.

France

No restrictions to the composition of the PVC material are included.

United States of America

NSF Standard number 14, section 3, item 3.00 General:

"Materials used in manufacture of pipe, fittings, valves, traps, joining materials and appurtenances covered by this Standard shall meet the public health and safety as well as performance requirements as established here in for the intended use or application. All such materials shall be manufactured in a manner which will prevent introduction of possible contamination thereto. Item 3.001 Such quality procedures and reports are deemed necessary to continued uniform quality of the materials and continued compliance with the applicable ASTM requirements for said material may be required.

Item 3.002 "The addition of innocuous tracers to materials covered by this Standard may be required when so recommended by the NSF Joint Committee on Plastics."

Item 3.003 "The manufacturer shall submit, at the time of requesting evaluation and qualification of a thermoplastic material and/or joining material, complete information for such material. When any change is made in the formule or in the source of supply of ingredients therein, such additional information shall also be submitted.

Said information shall be retained on a confidential basis."

Item 3.02 "Potable water application: Thermoplastic materials for pipe, fittings, valves, joining materials and/or appurtenances for potable water applications shall contain no ingredients in an amount which has been demonstrated to migrate into water in quantities which are considered toxic and shall conform to the specific requirements as stated in item 3.021 Toxicological and organoleptic - and 3.022 - Physical requirements.

Australia

The material from which the pipe is produced shall consist only of polyvinylchloride or modified polyvinyl chloride, to which shall be added suitable lubricants, pigments, stabilizers, and pastes thereof.

The total plasticizer content shall not exceed 1 part per 100 parts by weight of the PVC content, and the total additives shall not exceed 20 parts by weight of the PVC content.

South Africa

Pipes and fittings shall be of unplasticized polyvinyl chloride (uPVC). The additives shall be such as to impart opacity and to enable sound extrusions and injection mouldings to be made and shall not adversely affect the weldability or the long term mechanical strength. Clean rework material generated from the manufacturers production to this specification may be used.

The softening point, determined in accordance with 6.2 shall be not lower than 75°C in the case of pipes, and not lower than 72°C in the case of fittings.

Summarizing the data the next items can be stated:

1. Complete information on the composition of the material used for production must be submitted by the manufacturer to the testing agency before uPVC pipe can be tested according to existing specifications.
2. Based on the informations of the manufacturer, tests on toxicity are commonly restricted to the leaching of a restricted number of heavy metals which are known to be present in the uPVC. Sometimes organoleptic properties are included.

The NSF also includes materials such as compounders delivered by material suppliers.

3. Changes in the composition of raw materials commonly include new testing of the uPVC pipe produced. Commonly the manufacturer is obliged to submit data to the testing institute on beforehand.
4. Normal frequency of testing on toxicity amounts ^{to} ^{about} 1 time per year.
5. Basic data have to be marked on the outside of the uPVC drinkingwater pipe including the seal of approval.

6. The test methods for the determination of the leaching of toxic materials are mainly based on extraction test simulating the worst conditions to be expected in normal practice.

7. The French standards do not prohibit the use of toxic stabilizers however, no leaching of any substance from uPVC drinkingwater pipe is allowed.

No test methods for the leaching of substances are described. According to the Standards, test methods may be set up individually.

Concerning the leaching of lead and tin from uPVC drinkingwater pipe a draft test method nr. T 54-027 has been set up recently.

9. Discussion

- 1) The Consultants Group had before it a background paper, statements by participants and points of detail which developed during the course of the discussion. The information in these documents has been set down in the previous chapters of this report. However during the discussion ideas were developed and crystallized between the members and the major points are reported in this chapter and the recommendations of the Group in the final chapter.
- 2) The meeting discussed the development of plastics pipe technology. It was obvious that differences in outlook, particularly between the U.S.A. and parts of Western Europe had produced bodies of experience with divergent views. Heavy metal stabilizers used in the formulation of uPVC pipe products present a potential toxic hazard but the technology of the industry will eventually derive products using non toxic ingredients.

This change may occur over an appreciable time and toxicologists will need to take an active role in the testing and control of these products.
- 3) The development of National and International Standards for plastics pipe was seen by the Group to be in a dynamic state. Out of the 54 Member Bodies of the International Standards Organisation (ISO) 9 countries were known to have produced standards with toxicity clauses. Others were being drafted. These clauses specified different methods of extraction, pretreatment procedures, extraction fluids, sizes of samples and duration and temperature of extraction. Out of this jungle of specifications some order has to be made to assist the use of uPVC pipe, particularly in the developing countries. Standards are being drafted by ISO and it was agreed that National authorities concerned with health aspects should support through their National Standards Organisation the development of a uniform procedure based on ISO method for toxicity control, presently in an advance draft stage.
- 4) Detailed discussion of the wording of the latest draft ISO Standard ISO/DIS "B" (Appendix 2) revealed a misunderstanding of the mode of application of the standard. The title as presently drafted suggested that uPVC pipe could be made and used from which, say lead, could be continuously leached into water at concentrations of just below 0.3 mg/l lead. The value of the concentration of lead in

drinking water should be as low as possible and certainly below 0.1 mg/l lead. The specification should clearly indicate that the higher value (0.3 mg/l) will not persist.

- 5) Studies of the experience of water supply authorities with extensive networks of lead stabilized uPVC pipe did not support the existence of an actual toxic hazard from this source. Data in this report give results of continuous negligible lead concentrations in their systems.

A change in the title of the specification, to indicate the role of the specification to prove the fitness of the new product for its use in water supply networks, allowed the Group to reach a common understanding of the principles implied in the standard.

- 6) Points of detail in the ISO draft standard method for test ISO/DIS "A" (appendix 1) were discussed and proposals made to be passed to the relevant Technical Committee of ISO for modification of some points of detail. (Appendix 3). However the Group was of the opinion that the standard in draft form already provided a useful tool for the control of uPVC drinking water pipe in the factory and by the health authorities responsible for water supply.
- 7) Discussion centred on lead and organo-tin used as stabilizers in uPVC pipe and analytical methods were discussed for the analysing of extractant fluids in test conditions. The outstanding lack of agreement between WRA+KIWA on the one hand and NSF on the other was considered as arising from a discrepancy between the analytical methods used. Further interchange samples were to be tested to confirm the agreement reached during the meeting.
- 8) The Group was concerned however that other hazardous elements might be present in extracts. Information has been given in this report of cadmium present as impurity in a lead stabilizer. The Group suggested that cadmium and other toxic elements should be confirmed as being absent or at negligible low concentrations in extracts from fluids in uPVC pipes under test conditions.
- 9) The Group discussed the lack of toxicological data on the organo-tin compounds (example: dialkyl tin) commonly used in uPVC pipe formulations.

There was no data available to the Group on the mechanism of the release of the tin stabilizer and its degradation products to the extracting fluids. Limited experimental data on the release of tin stabilizer (measured as tin) was available as a private communication from Bulgaria which did however show the same high initial value and progressive reduction as noted with the lead stabilizer systems.

- 10) The organotin compounds had a wide variety of toxicities measured on the basis of acute effects. No data was available to the Group on the risk with long term exposure at low concentrations. It was agreed that research effort had to be put onto this area so that acceptable daily intake could be proposed for these compounds. This area was not covered by the terms of reference of the joint FAO/WHO Expert Committee on Food Additives nor by the WHO Expert Committee revising the WHO International Standards for Drinking Water.

10. Conclusions

- 1) The Consultants Group agreed that WHO and its constituent members should confirm and promote ISO specifications because they embody the combined experience of many industrialized countries and are available to those developing countries which do not yet possess an indigenous plastics pipe industry with all its supporting components.
- 2) The most recently published ISO documents for uPVC pipes for the transport of drinking water relating to toxicological hazards are Draft International Standards ISO/DIS "A" and "B" dated ...?... 1972. Copies are appended to this report (appendices 1 and 2).
- 3) The Consultants Group studied these documents and certain features of them call for comments, as follows, which should be transmitted to the ISO Technical Committee ISO/TC 138 for its attention.
- 4) The current title of document ISO/DIS "B" gives an incorrect impression of the scope of the standard and the Group suggested the following amended title:
"Maximum initial concentrations of lead and tin from extractability tests of new unplasticized polyvinyl chloride (PVC) pipes intended for drinking water supply".
The explanatory clauses within the standard should be amended as a consequence of the change of title.
- 5) The Group studied evidence of the long term use of uPVC and support the test levels as given in document ISO/DIS "B". They are of the opinion that uPVC pipe made and tested according to these draft standards will be fully capable of transporting water to the quality criteria in the WHO International Drinking Water Standards, 3rd Edition and revisions of the Standard expected after study of the 16th Report of FAO/WHO Expert Committee on Food Additives (1972).

- 6) Members of the Group had considerable experience in the application of uPVC pipes and they considered that some details of the test procedure given in document ISO/DIS "A" should be reconsidered by the ISO Technical Committee ISO/TC/138. The detailed points are given in appendix 3.
- 7) The ISO Draft Standards ISO/DIS "A" and "B" only refer to the extractability of lead and tin. The Group considered that cadmium, should be controlled in the ISO Standard as a potential hazardous element which must not occur in uPVC drinking water pipe formulations.

Considerations should be given to the inclusion of minimum limits for other toxic elements that might be associated with uPVC pipe production.
- 8) The Group considered the test methods that were available to test for lead and tin in the extraction fluids. A suitable method for lead should have a limit of detection of better than 0.1 mg/l Pb and a method for tin should have a limit of detection of better than 0.006 mg/l Sn.
- 9) The Group was concerned about the non-availability of good toxicological data for the organo-tin compounds (and their degradation products) which migrate from uPVC pipe into the drinking water.

Considerable data existed for toxic organo-tin compounds used for agricultural purposes but this was not specific to the pipe use. The Group strongly urged that toxicological and supporting research projects should be undertaken to provide the necessary information.
- 10) There is need for continuing study and report by the Consultants Groups on the toxicological hazards of new chemicals used in water supply situations. In this field the organo-tin compounds should be considered and recommendations made for their safe use.



DRAFT INTERNATIONAL STANDARD ISO/DIS "A"

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • ORGANISATION INTERNATIONALE DE NORMALISATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

This Draft International Standard was submitted
to Member Bodies on

Voting on this Draft International Standard
will terminate on

EXTRACTABILITY OF LEAD AND TIN OF UNPLASTICIZED POLYVINYL CHLORIDE (PVC) PIPES
FOR DRINKING WATER SUPPLY. TEST METHOD

UDC 621.643.29:678.743.22:628.1:615.9

ISO/TC 138
Secretariat Netherlands

EXTRACTABILITY OF LEAD AND TIN
OF UNPLASTICIZED POLYVINYL CHLORIDE (PVC) PIPES FOR DRINKING
WATER SUPPLY. TEST METHOD

1. SCOPE

This International Standard is intended to describe the method of test to be applied for the determination of the extractability of certain stabilizers of unplasticized PVC, to verify if the extracted quantities do not exceed a certain concentration.

2. FIELD OF APPLICATION

This test method applies to pipes of unplasticized PVC.
It only relates to the extractability of two types of stabilizers:

- lead salts,
- organic derivatives of tin, mainly dialkyltin C₄ and higher homologues.

3. PRINCIPLE

The pre-washing of test pieces during a fixed time.
The filling of the test pieces with water acidified with CO₂, and the analysis of the quantity of the extracted stabilizer after a fixed time.

Note 1: The methods to be used for the determination of the quantity of material taken into solution, are not laid down. They shall permit to carry out the analysis with an accuracy of 0.01 mg/l for lead and of 0.001 mg/l for tin.

4. APPARATUS

- A glass pipe,
- A glass cock,
- Stoppers,
- Distilled water, acidified with CO₂ at a concentration of 150 mg/l.

5. TEST PIECES

For each test: 3 pieces of the pipe, 500 mm of length, with an internal content at least equal to the volume of the extracting liquid, required to determine the amount of dissolved material with the required accuracy.

6. PROCEDURE

6.1 Pre-washing

6.1.1 Close one end of each test piece with a stopper, in the middle of which a glass pipe is fitted provided with a glass cock. The stopper should be of PE or of any other material which will not affect the results.

6.1.2 Place the test pieces vertically with the open end upwards.

6.1.3 Let tap water flow in such a way into the test pieces that the rate of flow, regulated with the aid of the cock, is equal to 3 m/min and in such a way that the test pieces are continuously filled with water.

6.1.4 Maintain the water flow during a fixed period between 1 and 6 hours.

6.1.5 At the end of this period, stop the water flow, remove the stoppers and rinse out the test pieces with distilled water.

6.2 Extractability test

6.2.1 Close one end of each test piece, which has been subjected to the pre-washing, with the aid of a stopper composed of a material that does not contain any toxic substances nor influence the analysis.

6.2.2 Fill each test piece with distilled water, acidified with CO₂ at a concentration of 150 mg/l.

Note 2: For each series of tests, a freshly made solution of distilled water, acidified with CO₂ shall be used.

Note 3: To prepare the CO₂ solution of 150 mg/l, it is practical to saturate a sufficient quantity of water with CO₂, to determine the content of CO₂ by means of a suitable method and then to mix the saturated solution with a calculated volume of carbon dioxide free distilled water.

Close the other end by means of a stopper and maintain the filled test pieces at 20 ± 5 °C for 48 hours.

6.2.3 1st extraction: At the end of 48 hours empty the water from the test pieces into suitable containers, and determine the quantity of lead, if this is the sample for lead determination.

6.2.4 2nd extraction: Fill the test pieces again, with a fresh solution of distilled water, acidified with CO₂ and maintain the test pieces, after having closed them again, at 20 ± 5 °C for 48 hours. At the end of this period pour the water out of the test pieces.

6.2.5 3rd extraction: Refill the test pieces for the third time under the same conditions as described for the preceding extractions. At the end of 48 hours empty the water into suitable containers and, dependent on the substance to be determined, proceed to the 2nd determination of the quantity of lead, or to the determination of the quantity of

EXPRESSION OF RESULTS

7.1 Lead

7.1.1 Calculate for the 3 test pieces the arithmetic mean of the quantities of lead found in the extracts after the first and the third extraction.

7.1.2 Express the results in mg/l, with an accuracy of 0.02 mg/l.

7.2 Tin

7.2.1 Calculate for the 3 test pieces the arithmetic mean of the quantities of tin found in the extracts after the third extraction.

7.2.2 Express the results in mg/l, with an accuracy of 0.004 mg/l.

8. TEST REPORT

The test report shall include the following indications:

8.1 complete identification of the pipe tested,

8.2 number of test pieces,

- 8.3 the method used for the determination of the quantity of lead in aqueous solution,
- 8.4 the method used for the determination of the quantity of tin in aqueous solution,
- 8.5 quantities of extracted lead for each test piece after the first and the third extraction,
- 8.6 the arithmetic mean of the extracted lead for the pipe after the first and the third extraction,
- 8.7 quantities of extracted tin for each of the test pieces after the third extraction,
- 8.8 the arithmetic mean of the extracted tin for the pipe after the third extraction,
- 8.9 details of the procedure which have not been provided for by this test method, and also the accidental circumstances which might have affected the results.

EXPLANATORY REPORT

of the ISO/TC 138 Secretariat (Netherlands) concerning

Draft International Standard ISO/DIS -Extractability of lead and tin of unplasticized polyvinyl chloride (PVC) pipes for drinking water supply. Test method.

proposed by Technical Committee ISO/TC 138 - Plastics pipes and fittings for the transport of fluids.

Work on this question was started by Working Group TC 5/SC6/WG3 - "General properties of plastics pipes" in 1961, and led to the Preliminary Draft 5/6/3 N229.

It was submitted for Letter Ballot to the Member Bodies of TC5/SC6 as Draft Proposal 5/6 N318-Extractability of lead and tin of unplasticized polyvinyl chloride (PVC) pipes. Test method".

The Draft Proposal was approved by 7 votes in favour, 4 against (Italy, Japan, Poland and Sweden), while France abstained from voting, see the Results of Voting, document 5/6 N369.

The comments were dealt with by Working Group TC 138/WG5¹⁾ and led to the following amendments:

- The field of application was extended to all lead salts (The Draft Proposal was limited to those of organic acids),
- The description of the test pieces "3 pieces of pipe with an internal content equal to . . ." was reworded to read "3 pieces of the pipe, 500 mm of length, with an internal content at least equal to . . ."
- The accuracy of the results was changed:
 - for lead from 0.01 into 0.02 mg/l,
 - for tin from 0.001 into 0.004 mg/l.

The Draft is now being submitted for simultaneous voting by the P-members of TC 138 and by all ISO Member Bodies (combined voting procedure) as a Draft International Standard.

¹⁾ Sub-Committee TC 5/SC 6 was converted into Technical Committee TC 138, in August 1970



DRAFT INTERNATIONAL STANDARD ISO/DIS "B"

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION-ORGANISATION INTERNATIONALE DE NORMALISATION-МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

This Draft International Standard was submitted
to Member Bodies on

Voting on this Draft International Standard
will terminate on

PERMITTED LEVELS OF LEAD AND TIN IN UNPLASTICIZED
POLYVINYL CHLORIDE (PVC) PIPES FOR DRINKING WATER
SUPPLY.

UDC 621.643.29:678.743.22:628.1:615.9

ISO/TC 138
Secretariat Netherlands

PERMITTED LEVELS OF LEAD AND TIN IN
UNPLASTICIZED POLYVINYL CHLORIDE (PVC) PIPES
FOR DRINKING WATER SUPPLY

1. OBJECT

The object of the present International Standard is to fix the maximum levels for the extraction of certain stabilizers from unplasticized PVC.

2. FIELD OF APPLICATION

It applies to unplasticized PVC pipes intended for the transport of drinking water.

3. REFERENCE

ISO....., Extractability of lead and tin of unplasticized polyvinyl chloride (PVC) pipes for drinking water supply-Test method.
(At present at the stage of Draft)

4. SPECIFICATION

Under the test conditions for extractability described in ISO....., the extracted quantities of lead and dialkyl tin, C₄ and higher homologues, should not exceed the following values:

4.1 LEAD

- after the first extraction: 1.0 mg/l
- after the third extraction: 0.3 mg/l

4.2 Dialkyl tin, C₄ and higher homologues, measured as tin

- after the third extraction: 0.002 mg/l.

EXPLANATORY REPORT

of the ISO/TC 138 Secretariat (Netherlands) concerning

Draft International Standard ISO/DIS - "Permitted levels of lead and tin in unplasticized polyvinyl chloride (PVC) pipes for drinking water supply"

proposed by Technical Committee ISO/TC 138 - Plastics pipes and fittings for the transport of fluids.

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Work on this question was started by Working Group TC 5/SC 6/WG 3 - "General properties of plastics pipes" in 1961, and led to the Preliminary Draft 5/6/3 N 218.

It was submitted for Letter Ballot to the Member Bodies of TC 5/SC 6 as Draft Proposal 5/6 N 296 - "Permitted levels of lead and tin in unplasticized polyvinyl chloride (PVC) pipes intended for the transport of potable water".

The Draft Proposal was approved by 8 votes in favour, 2 against (Japan and Switzerland), while France and Italy abstained from voting, see the Results of Voting, document 5/6 N 369.

The comments were dealt with by Working Group TC 138/WG 5 ¹⁾.

The Draft is now being submitted for simultaneous voting by the P-members of TC 138 and by all ISO Member Bodies (combined voting procedure) as a Draft International Standard.

1) Sub-Committee TC 5/SC 6 was converted into Technical Committee TC 138, in August, 1970.

Detailed comments by the Expert Group on ISO Draft International Standard ISO/DIS "A" which should be considered by ISO/TC 138.

- a). The prewash period in the standard procedure is set within wide limits of 1-6 hours. The Group considered that a shorter period should be used of $\frac{1}{2}$ -1 hours and that conditions of installation of new pipes should require the water networks be continuously flushed for a period of more than 1 hour to remove excessive toxic components that might be present on the pipe inner wall before the water is allowed to be used for human consumption.
- b). The test procedure to make 150 p.p.m. carbon dioxide solution for the extracting fluid is liable to error and the Group proposed that an alternative procedure of passing carbon dioxide into distilled water until the pH of water was 4.5 ± 0.1 pH should be used. At this pH range the carbon dioxide content could be approximately 150 p.p.m.
- c). The extraction temperature of $20 \pm 5^{\circ}\text{C}$ was considered to be of doubtful validity when applying the test to pipe to be used in tropical and arid countries where exposed pipe and its contents could be at temperatures of $40 - 45^{\circ}\text{C}$ for several hours. The Group was not able to make specific recommendations to cover this point but asked that this should be further studied by the ISO Technical Committee.
- d). The extraction times of 3 x 48 hours were considered to be inconvenient to use and alternatives that did not require 6 day working should be given in the final standard.

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Dr. Santema
VI. 1.4

Health Aspects Relating to the Use of Polyelectrolytes in
Water treatment for Community Water Supply.

Report of a Consultant Group

A Consultant Group met in the Hague from 8 to 12 February 1973, convened by the WHO International Reference Centre for Community Water Supply (IRC) to review health aspects of the use of polyelectrolytes in water treatment.

Mr. P. Santema, Director of the IRC opening the meeting, emphasized the importance of protecting drinking water quality in the context of increasing environmental contaminants and draw special attention to the need for surveillance of possible health hazards of new water supply materials.

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1. Introduction

The use of polyelectrolytes ^{*}) in water treatment as flocculants and flocculation aids is based on a long tradition. At first organic and inorganic polyelectrolytes of natural origin such as soluble starches, gelatins, tannins, sodium alginate and activated silica were used. Later the production of water soluble synthetic polymers resulted in an increase application of such materials in water treatment processes.

Polyelectrolytes are used in water treatment processes for the following purposes:

- a) as coagulants for the destabilization of colloids
- b) as coagulant aids for improvement of the floc characteristics
i in water i.e. colour and turbidity removal resulting in accelerated flocculation, improved floc stability, rapid sedimentation and improved water clarity.
- c) as filtration aids in order to promote filter operation at increased filtration rates with the same or even higher quality of the treated water;
- d) as a sludge thickening and conditioning aids to improve the dehydration and settling rates of solids from sludges in water treatment plants resulting in an improvement of the sludge filterability.

Polyelectrolytes have been used with success when the traditional water treatment processes proved to be ineffective during the seasonal decrease of water temperature, in the case of an overloading of the treatment plant during rainfall and floods and in cases of the treatment of heavily polluted waters.

An important limitation of a broader application of polyelectrolytes is the lack of a simple and reliable procedure for evaluating polyelectrolytes in laboratory tests before their application in full scale operation. In the same way, the lack of simple analytical

methods for the determination of the residual polyelectrolyte concentrations and concern as to the toxicity of the synthetic polyelectrolytes are also limiting their use.

Regarding the use of polyelectrolytes for water treatment purposes in developing countries, there may be some additional complications due to instability at the high air temperatures and high humidity of the tropical climates and bacterial degradation of solutions of polyelectrolytes based on natural products.

The Scientific and Technical Committee of the International Water Supply Association is preparing a "Manual on Application of Flocculants for Potable Water Purification at Municipal Water Works". In the manual will be dealt with the technical problems of the polyelectrolytes application as far as handling and technology of application is concerned.

From a public health viewpoint, the toxicity of synthetic polyelectrolyte is particularly important, because there is no doubt that natural polyelectrolyte such as activated silica, sodium alginate, starch products and cellulose derivations are in most cases non-toxic. Of the synthetic polyelectrolytes, products based on polyacrylamide, polyacrylic acid and acrylamide-acrylate and some types of cationic polyelectrolytes are most widely used in water treatment applications and most of the relevant toxicological studies have been made with such products.

1.2 THE NATURE AND CHEMICAL STRUCTURE OF POLYELECTROLYTES

Polyelectrolytes are generally water soluble polymers of organic or inorganic nature charged with ionised groups. Originally the most frequently used inorganic polyelectrolyte in water treatment, was the so called activated silica.

Activated silica is considered to be a solution of polymeric silicates which are formed by the partial neutralization of sodium silicate.

The characteristic properties of the activated silica are determined by the initial silica concentration, reaction time, reaction pH and the intensity of mixing. As a result of difficulties involved in the preparation of activated silica organic polyelectrolytes are being used more and more because of the simplicity of preparing and dosing their solutions. The organic polyelectrolytes are usually subdivided into three classes according to the electric charge of the macro-ions which are dissociated in water: resp. nonionic polymers, anionic polymers and cationic polymers. Nonionic polymers can be prepared as polyalcohols, polyamides and poly (N-vinyl heterocyclics).

Anionic water soluble polymers can be synthesised from phosphonic sulphonic or carboxylic acid substitution of long chain polymers. Cationic polymers can be prepared from the sulfonium or phosphonium substituted monomer compounds or by polymerization of ammonium substituted organics.

A substantial part of the polyelectrolytes used in water treatment processes are either of anionic or nonionic origin.

The structure of natural polyelectrolytes is mostly based on a polyalcoholic configuration corresponding with the natural cellulosic polymers.

The majority of the commercial synthetic nonionic and anionic polyelectrolyte products are based on polyacrilamide. Pure polyacrylamide is nonionic and prepared from the acrylamide monomer by polymerization. It is possible for example to prepare nonionic acrylamides with molecular weights up to 10 million. The polyacrylamide can be subjected to a controlled hydrolysis

which converts a part of the substituted carbon atoms to carboxylic groups. The resulting polymers will get an anionic character. The anionic acrylamide type polymers can also be prepared by the copolymerization of acrylamide and acrylic acid.

The nonionic and anionic polyelectrolytes are normally used as coagulant aids. As such that they speeds up the coagulation process, but they do not replace the metal slats which are acting as the primary coagulants. It also appears that a minimum molecular weight of the polymer is necessary for a succesfully coagulation. The limited minimum molecular weight is also depending on such factors as the relative number of charged groups, the degrees of branching of the polymeric structure, the charge of the colloidal particles and the ionic strength of the solution. The cationic polyelectrolytes may well be used in the future as primary coagulants but this use has not developed significantly at the present time as no technical or economic advantages have been demonstrated. A practical consequence of the ability of cationic polyelectrolytes to absorb specifically on negative colloids and neutralize the primary charge is that these materials do not require a large molecular weight to be effective in destabilization and they can be used in the absence of primary metal coagulants. Unfortunately some cationic polyelectrolytes, have relatively high toxicity.

1.3 Theory of the action and application of polyelectrolytes

The most acceptable model for the explanation of the ability of polyelectrolytes to destabilize colloidal dispersion seems to be provided by the bridging theory.

According to the bridging theory, a polyelectrolyte must contain chemical groups which can interact with adsorption sites on the surface of the colloidal particle. When a polyelectrolyte molecule comes into contact with a colloidal particle, some of the active groups are adsorbed at the particle surface. The pliable coiled threads remaining extended in the solution can attach other vacant adsorption sites of several colloidal particles. A particle-polyelectrolyte-particle complex is thus formed, in which the polyelectrolyte is serving as a bridge between the particles. Thus the optimum destabilization only occurs, when a small fraction of the available adsorption sites on the surface of the particles are covered and if the dosage of polyelectrolyte is sufficiently large to saturate the particle surface a restabilized colloid can be produced, since no sites are available for the formation of polyelectrolyte bridges.

On the basis of the bridging theory it can be explained that an effective destabilization and aggregation of colloids by polyelectrolyte dosing is often achieved with a polyelectrolyte having a similar charge as the particle. This theory is confirmed by the phenomenon that under certain conditions a system which has been destabilized and aggregated can be restabilized with extended agitation, giving rise to the breaking of particle polyelectrolyte bonds.

The practical consequences of the bridging theory are involved to ensure an optimal average dosage of polyelectrolyte but also to prevent a localized overdosing by a rapid mixing and the addition of the polyelectrolytes in a too diluted solution. On the other hand a prolonged intensive stirring can break the floc aggregates.

2. Control of polyelectrolytes in various countries

In 1970 the I.R.C. requested the Collaborating Institutions and other institutions in different countries for information with respect to the requirements or standards for polyelectrolytes application in water treatment, and on toxicological as well as on analytical procedures etc.

The resulting conclusions from this questionnaire which has been completed by 20 collaborating countries were as follows: Synthetic polyelectrolytes are at present rarely used in developing countries.

There are no standardized analytical methods for the determination of residuals of polyelectrolytes in water nor for the analyses of polyelectrolyte trade products.

The standards for the application of polyelectrolytes are in the U.S.S.R. and in Czechoslovakia based on the permissible concentration of the residual of the polyelectrolyte in the water. The Czechoslovak norm for the residual polyacrylamide product is fixed at 0.5 mg/l polyacrylamide whereas in the U.S.S.R. this norm is settled to the value of 2 mg/l. These standards are based on the information obtained from toxicological studies which have been performed by public toxicological agencies. In the U.S.A. the Technical Advisory Committee on Coagulant Aids and in the U.K. the Committee on New Chemicals for Water Treatment approve individual polyelectrolyte products on the basis of information obtained from the toxicological research carried out by the manufacturers. The data on chemical composition, purity, uniformity, stability, reaction properties, recommended levels of dosage, methods of application and in

particular data on toxicity of products are required for an approval. The guidelines given by the Environmental Protection Agency (U.S.A.) to manufacturers of coagulant aids, as to the information required for the evaluation of the acceptability of their products are given in Appendix 1.

In U.K. the manufacturer must submit the technological scheme of production as one of the basic data for obtaining approval and in the case of changing the technology of production the products have to be re-approved.

The following principles which have been adopted by the Committee on New Chemicals for Water Treatment are considered to be of the utmost importance.

1. Applications for consideration by the Committee of new products are only accepted from manufacturers. This ensures that full information on the product is available and that appropriate guarantees can be given. The only exception to this rule is when a product that has already been approved by the Committee is to be resold under a different trade name. In this case the company reselling the product has to guarantee that the new named product will never be other than the product already approved.
2. The manufacturer has to provide some evidence of the effectiveness of his product if this is an entirely new type of material. The object of this is to prevent the time of the Committee being taken up by considering useless products.
3. It is entirely the responsibility of the manufacturer to provide the Committee with appropriate toxicological information. The

role of the Committee is to consider this information, if necessary to request more information, then to approve or reject the product.

4. In considering possible hazards to health arising from the use of any particular chemical no allowance is made for the removal of that chemical in the treatment process as this can be affected by plant design and operator efficiency. In any case it has been shown that acrylamide monomer is not removed significantly in flocculation and filtration.

In the near future a scheme will be instituted in the U.K. in which water authorities using polyacrylamide based products will periodically send samples to the Department of the Environment to be checked for monomer content.

For polyacrylamide products the Committee on New Chemicals for Water Treatment of the U.K. requires that the product must not contain more than 0.05 percent monomer and that the dose of the products must not exceed 0.5 mg/l on average or 1 mg/l on any occasion.

In Germany a Commission was set up in 1971 to issue guidelines on the safe use of coagulant aids and to develop suitable test procedures. In the Netherlands a similar Committee is being established.

In setting limits for the levels of undesirable impurities in coagulant aids it is important to specify a satisfactory method of analysis for the contaminant in question. It has been found for example that some methods used for the determination of acrylamide in polyacrylamides may give very low results due to polymerisation of the acrylamide during extraction with a hot solvent (ref.).

In the U.K. the Committee on New Chemicals for Water Treatment have specified a method for acrylamide which overcomes this problem (ref.). This method is detailed in Appendix 2.

3. Toxicity of polyelectrolytes

A significant amount of toxicological data on polyelectrolytes has been submitted on a confidential basis by manufactures to the relevent committees in the U.S.A. and the U.K.

Details of a number of studies on the toxicity of the most widely used group of synthetic polyelectrolytes - those based on polyarylamide - have however been published.

The toxicity of polyacrylamide has been shown to be very low (6, 9, 10, 11, 21).

McCollister (10) for example carried out biochemical tests on the absorption, distribution and excretion of polymer in rats which indicated no or trace absorption from the gastrointestinal tract. From a two year feeding test with Separan NP10, a nonionic polyacrylamide and AP30, an anionic polyacrylamide, the laboratory animals (rats and dogs) tolerate 5-10% of these polyelectrolytes in their daily diet without harmful effects (10). Both products contained a maximum of 0.08% acrylamide. No effect levels of 500 mg/kgb.w/day (rats) and 700 mg/kgb.w/day (dogs) can be derived from this work. On the basis of the acrylamide content of the polymer fed, these no effect levels correspond to an acrylamide intake of 0.4 mg/kg/day for rats and 0.5 mg/kg/day for dogs.

In an investigation of the American Cyanamid Company (11) a polymer consisting of 90 percent acrylamide and 10 percent acrylic acid was fed to rats and dogs during a period of two years at dietary levels of 2.5, 5 and 10 percent for dogs. No animals died as a result of this intake of polymer.

Investigations on the toxicity of the Russian product PPA (no data are available on the monomer concentration) also show a low toxicity of the polyelectrolyte (9). The LD₅₀ of this product for white mice was fixed at a level of 12950 mg/kg day and at 11250 mg/kg day for rabbits. From the results of chronic experiments during a period of 10 months, it was concluded that a dose of 1.5 mg/kg day can be considered as the threshold concentration for warm blooded mammals.

Experience from the exposure of workers in factories proved that a concentration of 1 mg/m³ in air of polyacrylamide for a period of many years is without detectable toxicological effect. About 5 mg/day might be ingested by human subjects in such areas.

Acrylamide monomer, which may be present in commercial products to the extent of a few percent (15) has been shown to be highly toxic. Kuperman (13) and McCollister (14) reported an LD₅₀ for rats, guinea pigs and rabbits ranging from 150 to 180 mg/kg day. Trakhtman (9) gives the LD₅₀ for white mice and rabbits from 320.6 mg/kg day to 368 mg/kg day. Diagnostic signs of poisoning of the test animals resulting from excessive consumption of acrylamides include stiffness and weakness in the hind legs, loss of ability to control urinary retention, ataxia of front legs and inability of the test animals to stand. These neurological effects can occur when sufficient high dosages are given either once or repeatedly, by any route of administration. The cat was found to be most sensitive species with a "no effect" dosage of between 0.3 and 1.0 mg/kg day.

McCollister (14) concluded that for the exposure of the general public to acrylamide on a day-to-day basis, the total adsorption should not exceed 0,5 µk/kg day. This provides a large margin of safety (about 1000 fold).

No data of possible effects on reproduction, terratogenicity and mutagenicity are available, nor data on the metabolism of the monomer and possible combined effect of this substance with other chemicals of toxicological significance. Microamounts of which form the intake of man from the environment.

There are difficulties in the critical toxicological evaluation of residual monomer in drinking water in relation to the usual procedure of many WHO/FAO expert committees of setting an ADI (Acceptable Daily Intake) for microquantities of chemicals in food. Additional studies would be desirable for estimating such an ADI (metabolism of the monomer, 3 generation reproduction studies, teratogenicity, mutagenicity and other studies). Also the relationship between oral and percutaneous intake should be considered in the evaluation of the potential toxicological risk.

One of the few cationic polyelectrolytes, which has been certified by the U.S. Public Health Service Advisory Committee on Coagulant Aids in Water Treatment as safe for use in water treatment is Catfloc (1). Catfloc is a high molecular weight homopolymer of dimethyl diallyl ammonium chloride. Commercial Catfloc is a 15% aqueous solution of polymer solids. The polymer solids contain an average of 3% unpolymerized monomer but with this product the monomer is even less toxic than the polymer. The LD₅₀ of the monomer is 5600 mg/kg day while the LD₅₀ of polymer is 2800 mg/kg day (17).

In the U.S.S.R. a toxicological investigation of the cationic polyelectrolytes VA-2, VA-3, VA-2T, VA-3T has been carried out (20). VA-2 and VA-3 are products of ammonization of polystyrene by trimethylamine (VA-2) and by pyridine (VA-3). VA-2T and VA-3T

are products of ammonization of polyvinyltoluene by trimethylamine (VA-2T) and by pyridine (VA-3T). No data are given for the content of impurities in these products. Long term feeding studies (7 and 10 months) of white mice, white rats and guinea pigs indicated that VA-2 and VA-2T were the least toxic substances. The chronic test data proved that VA-2 and VA-2T at a dose of 1 mg/kg day have a toxicological effect on the animals, while at a dose of 0.1 mg/kg day this effect was temporal. At a dose of 0.02 mg/kg day no harmful effect could be established.

On the basis of these tests the VA-2 and VA-2T products have been approved at a concentration of 0.5 mg/l (26) as the maximum permissible concentration in water used for hygienic and domestic purposes.

4. The removal of polyelectrolytes in water treatment processes

In order to fully evaluate the toxic hazards arising from the use of polyelectrolytes it would be desirable to have data on the removal of these substances during water treatment. A number of methods for the determination of polyelectrolyte residuals have been reported in the literature (3, 15, 16, 18, 22, 23), but for the most part these are too insensitive or subject to interference to allow their use under practical conditions. Sontheimer (18) has reported data obtained on a pilot water treatment plant at Leipheim where the applied concentration of 0.3 mg/l polyacrylamide was decreased to 0.026 mg/l in the effluent of the coagulation clarifiers, finally to 0.01 - 0.002 mg/l in the effluent from the rapid sand filters and below 0.002 mg/l in the effluent after the activated coal filters. Similar experience has been reported by Hässelbarth (3); a residual concentration of the polyacrylamide product Sedipur TF of 0.005 - 0.003 mg/l in the effluent of the coagulation unit, whereas no detectable concentration in the effluent of the rapid filter could be found. The latter workers both used measurement of the effect on the setting rate of a standard kaolin suspension (3, 18, 22, 25), to determine the residual concentration of polyacrylamide. As far as the cationic polyelectrolytes are concerned, Black (19) reported that with appropriate coagulation the cationic polyelectrolyte could be removed to about 95%. Because of uncertainty as to the removal of polyelectrolytes in water treatment the best practice is to consider any toxic hazard on the basis of the applied dose of the chemicals. Using a method of determining acrylamide in water down to 0.1 µg/l (ref.) measurements have been made of the removal of acrylamide in water treatment (ref.). These have shown that effectively all

of the acrylamide applied to water in a polyacrylamide coagulant aid can be found in the filtered water. Laboratory experiments have indicated that acrylamide can be completely removed by the suitable application of an oxidative treatment e.g. ozone, chlorine potassium permanganate. No information is currently available on the toxicity of the reaction products of such oxidising agents with polyelectrolytes or their impurities.

5. Other uses of polyelectrolytes

Considerable quantities of polyelectrolytes are used in industrial solid liquid separation processes e.g. sand and gravel extraction, coal washeries, paper mills, and the products used are not normally subject to any control even in countries with an approval system for products used in water treatment. Thus the acrylamide monomer content of a potable water grade polyacrylamide may be restricted to less than 0.05% while products containing up to 1 or 2% monomer may be used for other purposes.

A recent survey of effluents from a number of industries has shown that these may obtain acrylamide at levels greatly in excess of those allowed in water for public supply.

Table 1

Effluent	Acrylamide concentration $\mu\text{g/litre}$
Colliery A Tailings Lagoon	42
Colliery B Tailing Lagoon	39
Colliery C Coal washing effluent lagoon	1.8
Colliery/coking plant effluent	0.74
Paper mill A treated effluent	0.47
Paper mill B treated effluent	1.2
Clay pit effluent	16
Sewage effluent (containing waste from chemical manufacturer using acrylamide)	1100

In considering the figures in Table 1 it should be borne in mind that on the basis of the specification of the Committee on New Chemicals for Water Treatment, the average level of acrylamide in potable water should not exceed $0.25 \mu\text{g/litre}$.

The possibility of other sources of exposure to the general public of polyelectrolytes cannot be ruled out polyacrylamides are used for example in the washing of prepacked foods and vegetables. Methylol acrylamide a compound having very similar toxicological properties to acrylamide is used in considerable quantities for the manufacture of adhesives. A method of grouting involving the injection underground of acrylamide with suitable polymerisation catalysts is being promoted by at least one major chemical company. In view of the hazardous nature of these materials a careful study of their use and possible impact on the environment is highly desirable.

6. Conclusions and recommendations

6.1 Polyelectrolytes for use as coagulant aids, filter aids, sludge conditioner and the like have a role in public water supply treatment. However water treatment plants managers and operators should be warned that these polyelectrolytes, if used unwisely, may have adverse physiological effects upon the individuals consuming such water.

In countries where adequate control and supervision cannot be given their use should be discouraged. Polyelectrolytes produced from natural compounds, such as starch, may not be hazardous but those produced by polymerization of man-made organic compounds will present a toxic risk in most cases not from the polymer itself, but from residues of the original monomer if this is present in appreciable quantities.

It is recommended therefore that the use of polyelectrolytes in water treatment should be studied with care. If they are to be used, then the naturally based polyelectrolytes should be chosen but if adequate plant supervision and adequate laboratory facilities are available to the Health Authorities and the Water Supply Authorities then the use of synthetic polyelectrolytes might be permitted.

6.2 Rigorous introductory procedures and continuing supervision of the use of polyelectrolytes both from natural and synthetic chemicals are in effect in the U.K., U.S.A. U.S.S.R. and other industrialized countries. In the U.K. and U.S.A. this control is exercised through a National Committee of experts.

It is recommended that such National Committees be set up before polyelectrolytes are to be used in water treatment processes.

The procedure adopted by the United States Environmental Protection Agency might be considered as a model procedure (full details are given in Appendix).

6.3 Polyelectrolytes are finding increased uses in situations other than water treatment- for example - sugar processing, vegetable washing, mineral processing, waste water treatment and soil stabilization. National Committees should see that special low toxicity grades of polyelectrolytes are specified and prescribed for these and other uses. For example, in the U.K.'s control procedure for polyacrylamide of potable watergrade, the residual monomer must be kept below 0.05% of the total product.

6.4 The national Committees should consider if toxic components in coagulantsaids are present in raw water sources. In existing National approval schemes it is assumed that the only source of the toxic components is from the added polyelectrolytes. It is urged that National and International organizations concerned with toxicological matters should be informed of this toxic hazard via the water route. Their recommendations for the control of similar compounds must take account of the use of polyelectrolytes in water treatment were this is applied.

6.5 If the procedures of control are set up as the U.S.A. EPA model then it is necessary for the National Committees to request manufacturers of polyelectrolytes to provide information on the composition, maximum recommended dosage under conditions of use and toxicity of the various components and additives of their particular product. The approval for the use of the product may be given after study of manufacturing and toxicological data by the National Committee. This procedure will assure that the possible toxic hazards are controlled within reasonable limits.

6.6 It is necessary for the controlling laboratories to be able to reliably determine trace concentration of toxic components in the polyelectrolyte itself. However, it is not absolutely necessary that the toxic component be determined in the treated water.

6.7 Present use of polyacrylamides relies on limited toxicological data for animals and on the information obtained during industrial exposure conditions.

It is recommended that further toxicological data be acquired for the establishment of Acceptable Daily Intake (ADI) of acrylamide monomer such as metabolic fate studies, three-generation reproduction studies, teratogenicity and mutagenicity studies.

6.8 It is recommended that National Committees should send their lists of approved products to the IRC so that the experience of the industrialized countries may be readily available to those using or about to use these products.

6.9 It is recommended that manufacturers be encouraged to make available, to the users of their product, as much information as possible on its chemical and toxicological quality.

APPENDIX 1

ENVIRONMENTAL PROTECTION AGENCY

GUIDELINES FOR THE INFORMATION NEEDED FOR EVALUATION OF ACCEPTABILITY OF NEW PRODUCTS AND FORMULATIONS INTENDED FOR USE AS

COAGULANT AIDS FOR WATER TREATMENT

INTRODUCTION

One of the primary concerns in the use of water coagulant aids is that they contribute no hazard to man's health; consequently, there must exist assurance that the benefits of the new technologies and new products are attained with minimal risk to man's health and well-being.

The Committee on Coagulant Aids for Treatment of Drinking Water serves as the mechanism for the review and acceptance or rejection of chemicals for treatment by coagulation of potable water on the basis of their safety for such use. The membership of the Committee consists of professionals in Toxicology, Chemistry, Water Treatment, and related fields.

Certain basic information is needed in order for the Committee to evaluate the acceptability of each coagulant aid for which approval is requested. These requirements are covered in Sections I and II. In no case will the Committee consider products without complete information on their composition. If the material is to be treated as confidential, the petitioner should indicate this preference, and his wishes will be respected.

Because coagulant aids are applied to water consumed under varied environmental conditions and for prolonged periods by the public, which includes individuals of all ages and susceptibilities, stringent safeguards for health protection must apply. The chemicals under consideration are not essential to the production of potable water but rather are useful and economic additives in water treatment. For these reasons, the Committee requires that the safety of low-exposure long-term use as well as higher-exposure shorter-term use of the proposed material be demonstrated by evidence that leave no reasonable basis for doubt.

The minimum for acceptable toxicologic data concerning all new products is a definitive study of the effects sustained by

experimental animals such that the results may be projected to man. This objective can rarely be achieved in less than one year of investigation. Section III lists suggested toxicologic studies. The minimum number of levels of concentrations in water (or other suitable media) to be administered to animals over a prolonged period is three: The concentration recommended for use, 10 times that concentration, and 100 times the recommended concentration.

If a material is known to be without harmful physiological effects on the basis of (a) controlled epidemiologic and toxicologic studies, (b) previously demonstrated acceptability, or (c) existence as a normal constituent of foodstuffs, some of the studies called for under Section III may be unnecessary. However, only minimum requirements are given, and it is not intended that they be construed as limiting the volume of data that should be developed in evidence of safety. Rather, it is more important that the investigations be tailored to fit to toxicological needs of the compound under test. For example, if it appears that the substance produces changes in the cellular elements of the blood, experiments should be so designed as to explore in some depth the nature of these changes by more sensitive and more specific techniques.

Toxicological investigations should be designed to produce information pertinent to the question of long-term safety of use of the product as a water treatment chemical. It should be appreciated also that the advice of qualified investigators should be sought in designing and performing the toxicologic studies.

Three (3) copies of all petitions should be directed to:

Secretary, Committee on Coagulant Aids
for Treatment of Drinking Water
Division of Water Hygiene
Environmental Protection Agency
5555 Ridge Avenue
Cincinnati, Ohio 45213

The petitioner will be notified directly as to the decision of the Committee within 30 to 90 days after submission of all data.

I. Chemical Properties

A. Composition

1. Physical and chemical composition (names, structures, and quantities) of constituents of the product.

2. All pertinent physical and chemical properties and specifications for ingredients of the commercial product, including lipid solubility and molecular weight distribution.
 3. If the substance is a polymer: a detailed description of methods used to characterize the products and assure its uniformity, including monomer content (%).
 4. Analytical methods for determination of residues of both polymer and monomer in water, including information on sensitivity, accuracy, and precision.
- B. Impurities, nature and amounts, including heavy metals.
 - C. Data demonstrating uniformity of product and description of quality control processes.
 - D. Stability in storage.
 - E. Reaction in water, including possible changes at elevated temperatures such as may be encountered in domestic water heaters, and at pH values from 5.0 to 11.0, and characterization of degradation production.
 - F. Reaction with other water treatment chemicals, such as, chlorine, and with known contaminants of drinking water such as heavy metals and characterization of reaction products.
 - G. Data on residues of monomer and polymer remaining in water after treatment under conditions of use not only when additional water treatment is used, but also when no other water treatment is used.
 - H. All trade and proprietary names.
 - I. Uses in other edible materials and amounts proposed or approved by other Agencies should be stated.
 - J. Label of product as sold.

II. Conditions of Use

- A. Recommended levels of dosage.
- B. Method of application including industrial experience relating to hazards and safe practices in handling.

- C. Dose-response data relating concentration of the product in water with the ability to coagulate suspended and dissolved material in waters having different chemical characteristics.

III. Evidence of Toxicity

The following types of experiments are commonly undertaken to develop information necessary to judge the acceptability of the product from the standpoint of human health. It is not intended that all procedures given below are required in each instance or that additional studies may not be required in some cases. Emphasis should be placed on studies that demonstrate high sensitivity, high specificity, and clinical relevance. Decisions on such questions should be made by competent investigators. Some procedural detail is given to provide some degree of uniformity in information submitted to the Committee on various products to aid its work of evaluation.

If the product is a polymer, these studies should be conducted on the monomer as well as the polymer, if feasible. These investigations should be designed to establish differences in susceptibility, if any, according to sex, species (rodent and non-rodent), age, and disease status. Since the goal is to project the results to biological responses in the human population, efforts must be made to include a significant number of animals in each group in order to have some basis to judge the frequency of response. If the product is administered with food - rather than in drinking water or by gavage - it is essential to establish that, (1) the product is stable and does not undergo chemical change and, (2) the effect level obtained under these conditions does not differ significantly from that recorded with water as the vehicle.

The information submitted should be presented in the form of data that has been subjected to appropriate statistical treatment (for example: means, ranges, standard deviations, standard errors, confidence limits, significance tests, etc.). The use of tabular and graphic forms is encouraged as means of organization and clarification.

If pertinent toxicologic and epidemiologic data have been previously reported in the scientific literature, the appropriate citations may be submitted in lieu of duplicating those studies.

A. Required Studies

1. Acute (single dose) Toxicity

a. Purposes:

- (1) To establish the LD 50 by oral and other routes in animals to permit relative toxicity ratings with known substances.
- (2) To characterize the slope of the dosage-response curve to permit more specific estimation of safe doses.
- (3) To note type, time of onset, severity, and duration of toxic signs and symptoms; to determine cause of death and organ damage.

b. As indicated from conditions of use, the acute toxicity of the product should be determined by one or all of the routes of administration listed below.

- (1) Oral LD 50. Use of published (standard) methods of procedure are suggested (J.T. Litchfield, Jr., and F.W. Wilcoxon, "A Simplified Method of Evaluating Dose-Effect Experiments," J. Pharmacol. Exptl. Therap. 96:99, 1949). In the case of mixtures of substances, the acute toxicity of the entire mixture should be determined, as well as the major contributor(s) to the toxicity.

Observation time: 2 weeks.

Animals: Mice, rats, and guinea pigs;
10 animals per dose

(2) Cutaneous toxicity - determination of:

- (1) Degree of absorption through the skin and extent of systemic effects.
- (2) Primary irritant effect.

- (3) Sensitizing properties. The standard method of Draize et al. (J. Pharmacol. Exptl. Therap. 82:377, 1944), is acceptable. The results of human experience are preferable and should be submitted, if available. Serious consideration should be given to clinical trials.

Animals: Guinea pigs and rabbits; 5 animals per dose.

- c. Ocular toxicity. Determination of irritation and injury (according to method of J.H. Draize "Dermal Toxicity" in Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics, Association of Food and Drug Officials of the U.S., Topeka, Kansas, 1965.)
- d. Potentiation Studies. Enhancement of sum of the individual effects caused by the administration of 2 or more chemicals to the same organism. Combination of product with environmental analogs, with heavy metals commonly found in water and with other water treatment chemicals.

2. Metabolism Studies

Purpose: To generate definitive information on the degree of absorption, extent of distribution, storage, tissue localization, metabolism, half-life in the organism, routes of excretion, and nature of excretory products. Such investigations, as determination of the rate of excretion following the administration of single or repeated doses at levels selected to be non-injurious to either kidney or gastro-intestinal tract, may provide helpful information in deciding potential risks from long continued exposure.

The manner and rate of absorption of an ingested substance can be highly informative, and at times, completely definitive. If, for example, it can be shown by radio-tracer, or other suitably sensitive technique, that the ingested substance under test is not absorbed, this fact in general will eliminate the need to carry out further tests

other than those to determine, (a) whether the substance is an irritant to the gastro-intestinal tract or, (b) whether it may prevent absorption of essential micro-nutrients.

The design of the experiments should incorporate single and multiple dosage schedules in order to assess possible storage and cumulative effects. At least 2 animal species should be used in order to detect inter-species differences. All vital organs of the experimental animals should be assayed for residues of the test material at varying times after cessation of exposure.

B. Recommended Supplemental Studies

If reliable information derived from human experience in the production, handling, and use of the material or from the administration of the coagulant aid to man is available, such information should usually take precedence over comparable data from laboratory animals. However, if such information is lacking and depending upon the type of responses obtained in the Required Studies (A.1. and A.2.), careful consideration should be given to conducting the following studies in order to obtain further information about the toxicity and possible human health effects of the coagulant aid. In order to obtain pertinent data, these studies should be tailored to the in-depth investigation of the toxic responses, as well as to the elucidation of deleterious effects resulting from chronic exposure.

1. Chronic Toxicity - Oral

- a. Purpose: Chronic oral toxicity tests are designed to provide data adequate to evaluate the safety of substances that may be ingested by man. When metabolic pathways are not known and/or unproductive of simple and safe explanations and where subacute toxicity tests have produced only minor effects, chronic toxicity tests should be carried out on the proposed chemicals. Chronic tests in contrast to subacute studies should determine with relative certainty that we are not encountering a case where the effect of exposure to a small amount of a compound for a long time differs markedly from an exposure to a large amount of the chemical for a short time. The chronic experimental data generated should be sufficient to establish a "no effect" dosage with

confidence. This "no effect" level can then be used to establish the definite margin of safety.

b. Animals:

- (1) Rats, weanlings, 50 (25 of each sex) per level with an equal number of controls. A larger number of rats per group will aid in the interpretation of results and therefore, reduce the possible risks of approving the use of a toxic substance or of missing a safe compound. If animals are to be sacrificed prior to the end of the study, the number of animals should be increased accordingly.
- (2) Dogs, under 1 year of age, 8 (4 of each sex) per level with an equal number of controls. Since there should be a minimum of 4 dogs remaining in each group at the termination of the experiment, the exact number used at the beginning depends upon the desirability of sacrificing animals during the experimental period and the accepted risk of losing animals from natural causes.

c. Duration: One to two years.

d. Levels of test material: Minimum of 3 test levels and a control.

- (1) One level at 10 times the concentration intended for use, or a "no effect" level, whichever represents the higher concentration.
- (2) One level at 100 times the concentration intended for use; or ten times the "no effect" level, whichever represents the higher concentration.
- (3) A level designed to produce mild adverse effects during the course of the experiment.
- (4) Control, no product added, vehicle only.

e. Criteria for toxicity:

- (1) Changes in body weight, appearance, growth, food consumption, and ability to reproduce.
- (2) Hematologic and biochemical parameters.
- (3) Gross- and histo-pathologic changes of organs of fatally poisoned animals and of those sacrificed for examination.
- (4) Alteration of activity of specific enzymes (e.g., cholinesterase, hepatic microsomal oxidases, etc.), if applicable.
- (5) Other criteria as indicated.

2. Carcinogenicity Studies

- a. Purpose: To determine if the coagulant aid is carcinogenic when ingested.
- b. Animals: Mice or rats. Ordinarily young animals are used; however, animals 10 to 12 months of age may be used.
- c. Duration: 12 months
- d. Levels: (Same as for B.l.d.).

3. Mutagenicity Studies

- a. Purpose: To determine whether the material produces genetic mutations deleterious to the basic functions of the organism.
- b. Methods: A number of techniques exist to test mutagenic potential. These include the Dominant Lethal Test, Cytogenetic Studies in Cultured Mammalian Cell Lines, Cytogenetic Evaluation from Bone-Marrow Preparations of Treated Animals, Host-Mediated Studies, and Induction of Forward-Reverse Mutations in Cultures Mammalian Cell Lines. There is no preference as to the use of any of these or other tests. However, it should be noted that some of the tests can be readily incorporated into the design of chronic toxicity studies.

c. Levels: (Same as for B.l.d.)

4. Teratogenicity Studies

a. Purpose: To demonstrate any effects upon fertility, ability to reproduce, size of litters, litter survival, etc., and to determine teratogenic and other fetal toxic effects.

b. Animals:

(1) Mice or rats.

(2) Rabbits.

c. Duration: Through the F2 generation.

d. Levels: (Same as for B.l.d.)

IV. Change of Trade Name or Product Designation Only

A. Repackaging of one previously approved product, the following are required:

1. Written testimony from the manufacturer and distributor to the effect that the product is the same in composition and quality as that previously approved, that the original manufacturing processes have not been markedly altered, and that the repackaging process does not adulterate the product.
2. Recommended levels of dosage under new trade name.
3. Label of the product as sold.

B. Repackaging of combination of two or more previously approved products, the following are required:

1. Written testimony from the manufacturer(s) and distributor to the effect that the products are the same in composition and quality as those previously approved, that the original manufacturing processes have not been markedly altered, and that the repackaging process does not adulterate the product.

2. The data from at least three batches of the new combination to demonstrate uniformity of the product.
3. Recommended levels of dosage of combination under new trade name.
4. Label of product as sold.
5. Acute potentiation studies combining both products (see Section III.A.1.b.(4)) by the intraperitoneal and oral routes.

ENVIRONMENTAL PROTECTION AGENCY

APRIL 1972

REPORT ON COAGULANT AIDS FOR WATER TREATMENT

On the basis of information submitted by the manufacturers and/or distributors, the Environmental Protection Agency has concluded that the following additional products may be used in water treatment without adverse physiological effects on those using the water, when applied in the concentration recommended by the manufacturers and/or distributors and provided the products continue to meet the quality specifications furnished.

<u>MANUFACTURER AND/OR DISTRIBUTOR</u>	<u>PRODUCT</u>	<u>MAXIMUM CONCENTRATION RECOMMENDED - mg/l</u>
Allied Colloids, Inc. One Robinson Lane Ridgewood, N.J. 07450	Percol LT-20	1
	Percol LT-22	1
	Percol LT-26	1
	Percol LT-29	1
American Cyanamid Co. Wayne, New Jersey 07470	MAGNIFLOC 573-C	10
	MAGNIFLOC 575-C	10
	MAGNIFLOC 577-C	10
	MAGNIFLOC 579-C	10
Betz Laboratories, Inc. Somerton Road Trevose, Pa. 19047	Betz Polymer 1150P	1
	Betz Polymer 1250P	1
	Betz Polymer 1160P	1
	Betz Polymer 1260P	1
Commercial Chemical Products, Inc. 11 Paterson Avenue Midland Park, N.J. 07432	Speedifloc #2	5
Drew Chemical Corp. 701 Jefferson Road Parsippany, N.J. 07054	AMERFLOC 265	1
	AMERFLOC 275	1
	AMERFLOC 307	1
	DREWFLOC 4	5

<u>MANUFACTURER AND/OR DISTRIBUTOR</u>	<u>PRODUCT</u>	<u>MAXIMUM CONCENTRATION RECOMMENDED - mg/l</u>
E. I. DuPont de Nemours and Company Eastern Laboratory Gibbstown, N.J. 08027	Carboxymethyl- cellulose	1
Henry W. Fink & Co. 6900 Silverton Avenue Cincinnati, Ohio 45236	No. 116 Kleer Flocc No. 119 Kleer Flocc	1 5
James Varley & Sons, Inc. 1200 Switzer Avenue St. Louis, Missouri 63147	VARCO-FLOCC	150

The Environmental Protection Agency emphasizes that its findings bear only on the health aspects of the use of these products in drinking water treatment and do not constitute endorsement or indicate effectiveness for the proposed use.

A fish kill was reported to have been caused by a coagulant aid that was used to treat a water impoundment for removal of turbidity. Some of the products listed may kill fish at or below maximum recommended concentration. The review of the suitability of these products is confined to their use in drinking water treatment. Information on fish toxicity, biointensification and biodegradability will be necessary for other types of application, and users should obtain such information from the manufacturers.

The total list of products reviewed in the past and found to be suitable for use in water treatment, and that the manufacturer and/or distributor still want to have listed, follows.

<u>MANUFACTURER AND/OR DISTRIBUTOR</u>	<u>PRODUCT</u>	<u>MAXIMUM CONCENTRATION RECOMMENDED - mg/l</u>
Allied Colloids, Inc. One Robinson Lane Ridgewood, N.J. 07450	Percol LT-20	1
	Percol LT-22	1
	Percol LT-24	5
	Percol LT-25	5
	Percol LT-26	1
	Percol LT-29	1
Allstate Chemical Co. Box 3040 Euclid, Ohio 44117	ALLSTATE NO. 2	3.0
	ALLSTATE No. 6	1
Allyn Chemical Co. 2224 Fairhill Road Cleveland, Ohio 44106	Claron	1.5
	Claron #207	2
American Cyanamid Co. Berdan Avenue Wayne, N.J. 07470	Superfloc 127	1
	Magnifloc 521-C	10
	Magnifloc 570-C	10
	Magnifloc 571-C	10
	Magnifloc 573-C	10
	Magnifloc 575-C	10
	Magnifloc 577-C	10
	Magnifloc 579-C	10
	Magnifloc 845-A	1
	Magnifloc 846-A	1
	Magnifloc 847-A	1
	Magnifloc 860-A	1
	Magnifloc 971-N	1
	Magnifloc 972-N	1
Magnifloc 985-N	1	
Magnifloc 990-N	1	
Atlas Chemical Industries, Inc. Wilmington, Del. 19899	SORBO	20
Berdell Industries 28-01 Thomson Avenue Long Island City, N.Y. 11101	Berdell N-489 Flocculant	1
	Berdell N-821 Flocculant	1
	Berdell N-902 Flocculant	1

<u>MANUFACTURER AND/OR DISTRIBUTOR</u>	<u>PRODUCT</u>	<u>MAXIMUM CONCENTRATION RECOMMENDED - mg/l</u>
Betz Laboratories, Inc. Somerton Road Trevose, Pa. 19047	Betz Polymer 1100P	1
	Betz Polymer 1110P	1
	Betz Polymer 1120P	1
	Betz Polymer 1130P	1
	Betz Polymer 1150P	1
	Betz Polymer 1160P	1
	Betz Polymer 1200P	1
	Betz Polymer 1205P	1
	Betz Polymer 1210P	1
	Betz Polymer 1220P	1
	Betz Polymer 1230P	1
	Betz Polymer 1250P	1
	Betz Polymer 1260P	1
	Poly-Floc 4D	25
Bond Chemicals, Inc. 1500 Brookpark Road Cleveland, Ohio 44109	Bondfloc No. 1-101	5
The Burtonite Company Nutley, N.J. 07110	Burtonite #78	5
Calgon Corporation P. O. Box 1346 Pittsburgh, Pa. 15222	Coagulant Aid #2	1
	Coagulant Aid #18	15
	Coagulant Aid #233	1
	Coagulant Aid #243	1
	Coagulant Aid #253	1
	Coagulant Aid #961	5
	Cat-Floc	7
Cat-Floc B	10	
Commercial Chemical Products, Inc. 11 Paterson Avenue Midland Park, N.J. 07432	Coagulant Aid Speedifloc #1	10
	Speedifloc #2	5
Dearborn Chemical Div. W. R. Grace & Co. Merchandise Mart Plaza Chicago, Ill. 60654	Aquafloc 408 (liquid)	50
	Aquafloc 409	1
	Aquafloc 411	2
	Aquafloc 422	1

<u>MANUFACTURER AND/OR DISTRIBUTOR</u>	<u>PRODUCT</u>	<u>MAXIMUM CONCENTRATION RECOMMENDED - mg/l</u>
Dow Chemical U.S.A. Barstow Building 2020 Dow Center Midland, Mich. 48640	Dowell M-143	5
	PEI-1090	5
	Purifloc A-22	1
	Purifloc A-23 (PWG)	1
	Purifloc C-31	5
	Purifloc N-17	1
	Separan AP-30	1
	Separan AP-273 Premium	1
	Separan NP-10 Potable Water Grade	1
	SA-1704.2	1
*XD 7817	1	
Drew Chemical Corp. 701 Jefferson Road Parsippany, N.J. 07054	Drewfloc 1	1:8 Alum; 0.5:10 Lime**
	Drewfloc No. 3	3
	Drewfloc No. 21	5
	Drewfloc 922	10
	AMERFLOC 265	1
	AMERFLOC 275	1
	AMERFLOC 307	1
	Drewfloc 4	5
DuBois Chemicals Div. of W.R. Grace & Co. 3630 E. Kemper Road Sharonville, Ohio 45241	FLOCCULITE 550	2
E. I. DuPont de Nemours and Company Eastern Laboratory Gibbstown, N.J. 08027	Carboxymethyl- cellulose	.1
Henry W. Fink & Co. 6900 Silverton Ave. Cincinnati, Ohio 45236	No. 102	1
	No. 109 Kleer-Floc	1
	No. 116 Kleer Floc	5
	No. 119 Kleer Floc	1
	No. 730 Kleer-Floc	1
	No. 735 Kleer-Floc	1
Gamlen Sybron Corp. 321 Victory Avenue S. San Francisco, Calif. 94080	Gamlose W	5
	Gamlen Wisprofloc 20	5
	Gamafloc NI-702	4

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/l
Garrett-Callahan 111 Rollins Road Millbrae, Calif. 94031	Coagulant Aid 72A Coagulant Aid 74B Coagulant Aid 76 Coagulant Aid 76A Coagulant Aid 78B Formula 70A Formula 73 Formula 74E	50 30 40 50 50 50 50 20
General Mills Chemicals 4620 W. 77th Street Minneapolis, Minn. 55435	SuperCol Guar Gum Guartec F Guartec SJ	10 10 10
Hercules, Inc. 910 Market Street Wilmington, Del. 19899	Carboxymethyl- cellulose Hercofloc 818 (Potable Water Grade) Hercofloc 821 (Potable Water Grade)	1 1 1
Frank Herzl Corp. 299 Madison Avenue New York, N.Y. 10017	Perfectamyl A5114/2	10
Illinois Water Treat- ment Co. 840 Cedar Street Rockford, Ill. 61102	Illco IFA 313	10
Kelco Company 8225 Aero Drive San Diego, Calif. 92123	Kelgin W Kelcosol	2 2
Key Chemicals 4346 Tacony Philadelphia, Pa. 19124	Key-Floc-W	25
Metalene Chemical Co. Bedford, Ohio 44014	Metalene Coagulant P-6	5
The Mogul Corporation 20600 Chagrin Blvd. Cleveland, Ohio 44122	Ecco Suspension Catalyzer 146 MOGUL CO-980 MOGUL CO-982 MOGUL CO-983 MOGUL CO-985 MOGUL CO-986	3.5 2 1.5 1 3.5 5

<u>MANUFACTURER AND/OR DISTRIBUTOR</u>	<u>PRODUCT</u>	<u>MAXIMUM CONCENTRATION RECOMMENDED - mg/l</u>
Nalco Chemical Co. 6216 W. 66th Place Chicago, Ill. 60638	Nalcolyte 110A	5
	Nalcolyte 607	7
	Nalcolyte 671	1
	Nalcolyte 7870	1
	Nalcolyte 8170	1
	Nalcolyte 8173	1
	Nalcolyte 8175	1
Narvon Mining & Chem. Co Affiliate of Irl Daffin Assoc. Keller Ave. & Fruit- ville Pike Lancaster, Pa. 17604	Sink-Floc Z3 and AZ-3	10
	Sink-Floc Z4 and AZ-4	10
	Sink-Floc Z5 and AZ-5	10
	Zeta-Floc C	20
	Zeta-Floc K	20
	Zeta-Floc O	20
National Starch & Chem. Corp. 1700 W. Front Street Plainfield, N.J. 07063	Floc-Aid 1038	5
	Floc-Aid 1063	5
O'Brien Ind., Inc. 95 Dorsa Avenue Livingston, N.J. 07039	Q'B Floc	10
Oxford Chemical Div. Consolidated Foods Corp. P. O. Box 80202 Atlanta, Ga. 30341	OXFORD-HYDRO-FLOC	10
W. A. Scholten's Chem- ische Fabrieken M.V. Foxhol, Postbus 1 The Netherlands	Wisprofloc P	5
Standard Brands Chem. Ind., Inc. Div. of Std. Brands P. O. Drawer K Dover, Del. 19901	TYCHEM 8035	1
A. E. Staley Mfg. Co. P. O. Box 151 Decatur, Ill. 62525	HAMACO 196	5

<u>MANUFACTURER AND/OR DISTRIBUTOR</u>	<u>PRODUCT</u>	<u>MAXIMUM CONCENTRATION RECOMMENDED - mg/l</u>
Stein, Hall & Co., Inc. 605 Third Avenue New York, N.Y. 10016	Hallmark 81	1
	Hallmark 82	1
	Jaguar	0.5
	MRL-14	1
	MRL-22	1
	Polyhall M-295 P.W.	1
James Varley & Sons; Inc. 1200 Switzer Avenue St. Louis, Missouri 63147	VARCO-FLOC	150
W. E. Zimmie, Inc. 810 Sharon Drive Westlake, Ohio 44145	Zimmite ZM-100	1
	Zimmite ZC-301	130
	Zimmite ZT-600	1
	Zimmite ZT-601	1
	Zimmite ZT-603	1

* Name Change

**One part of Drewfloc to 8 parts of alum when used simply as an aid in alum coagulation, and 0.5 mg/l of Drewfloc to 10 mg/l of lime when used in connection with lime softening.

APPENDIX 2

THE DETERMINATION OF ACRYLAMIDE IN POLYELECTROLYTES

1. INTRODUCTION

Work in these laboratories has indicated serious discrepancies in the amounts of monomer extracted from acrylamide polymers and co-polymers by various extraction methods. The extraction procedure detailed in Sect. 2 of this report has been found to be satisfactory, giving identical results to analyses performed on aqueous solutions of polyelectrolytes. However, analysis of aqueous extracts by gas chromatography is normally only satisfactory if the polymer contains 0.5% acrylamide or more.

A gas chromatographic procedure for the determination of acrylamide was used in studying the efficiency of different methods of extraction and full details of this are given in Sect. 3 of this report. Although the recommended extraction procedure was designed to precede analysis by G.L.C., it may be used with slight modification with other types of analysis as mentioned in Sect. 2.2.

2. EXTRACTION OF ACRYLAMIDE FROM POLYELECTROLYTES

2.1. Procedure

Weigh out 1 g of polymer into a 1 oz McCartney bottle, add 10 ml (note 1) of a 20% water 80% methanol mixture (note 2) and screw down the cap firmly. Shake to disperse the polymer and transfer to a Microid flask shaker. Clamp horizontally, and shake vigorously for 24 hours (note 3). Allow the polymer to settle and take an aliquot for analysis (notes 4 and 5).

2.2. Notes

1. The polymer to solvent ratio is not critical, identical results were achieved using 2 g polymer to 10 ml solvent and 0.2 g polymer to 10 ml solvent. 1 g polymer to 10 ml solvent was the highest polymer to solvent ratio which gave a mobile slurry with all polymers tested.
2. Higher percentages of water in methanol give faster extraction of acrylamide but caused some polymers to gel. Lower percentages did not extract all the acrylamide. A 20% water 80% methanol mixture gave complete extraction of acrylamide, without causing any of the polymers tested to gel.
3. It is essential that no aggregation of the polymer particles is allowed to take place or poor extraction will result. The above vessel (McCartney bottle) and shaking methods were found applicable to all polymers tested. Some polymers were completely extracted in considerably less than 24 hours, but no polymer tested showed any increase in acrylamide recovery after this time.
4. Larger scale extractions will be necessary for some other types of acrylamide analysis. This is feasible provided that the above recommendations are adhered to, note 3 being particularly important.

5. Extracts deteriorated if stored on the bench for more than one or two days. Samples stored in a refrigerator, however, were still satisfactory after one week. Longer periods of storage were not tested.

3. THE ANALYSIS OF ACRYLAMIDE BY GAS CHROMATOGRAPHY

3.1. Instrument

Perkin-Elmer F11 equipped with flame ionisation detector, and glass columns. On-column injection was achieved by use of a 10 μ l Hamilton microsyringe (5 in. needle).

3.2. Column and conditions

Glass column 1 metre long by 3 mm internal diameter packed with 60-80 mesh, acid washed, dichlorodimethylsilane treated Chromosorb W, supporting 20% by weight of Carbowax 20M. The column is run at 170°C and 32 ml/min of N₂. Before use the column must be conditioned by running at 200°C (32 ml/min N₂) overnight.

3.3. Standard solutions

Solutions of acrylamide in a 20% water 80% methanol mixture made up at 0.01, 0.05, 0.2 and 2 mg/ml respectively.

3.4. Calibration of chromatograph

Inject 5 μ l of each of the above standards into the chromatograph (on-column injection) using amplifier attenuation settings to give peaks not greater in height than half scale. (On the above instruments 5 x 1, 20 x 1, 1 x 10² and 10 x 10² respectively). These injections correspond to 0.05, 0.25, 1.0 and 10.0 μ g acrylamide.

Estimate the areas of the peaks by multiplying the peak height by the peak width at half the peak height. The second parameter should be measured parallel to the sloping baseline constructed from the tail of the solvent peak, as shown in Fig. 1. This is important with the smallest amount of acrylamide injected.

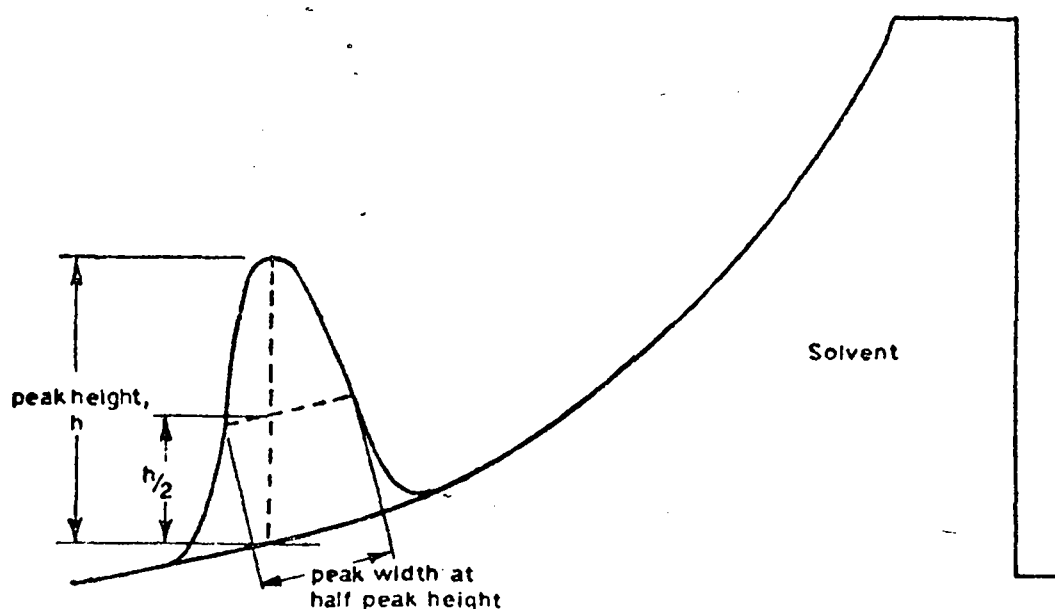


FIG. 1. ESTIMATION OF PEAK AREA

The relationship between amount of acrylamide injection (μg) and peak area (sq cm at an attenuation of 1) is non-linear on the above instrument, but an excellent straight line calibration can be achieved by the use of a log-log plot. This graph will cover monomer in polymer concentrations of 0.01 to 2% using 1 g polymer to 10 ml extracting solvent (20% water 80% methanol mixture).

3.5. Estimation of acrylamide in a sample extract

Inject 5 μ l of extract and estimate the area of the acrylamide peak using the above method. An attenuation setting should be chosen such that the peak height is less than half scale on the recorder. Read off the quantity of acrylamide present in the 5 μ l injection from the calibration graph. For a polymer to solvent ratio of 1 g to 10 ml the percentage of acrylamide in the polymer may be calculated as follows:

$$\% \text{ monomer} = 0.2X$$

where X = μ g of acrylamide in the injection.

3.6. Notes

1. On-column injection may not be necessary, but with the above instrument it gave the best peak shapes.
2. Other G.C. columns were tested:
 - 10% neopentylglycol succinate/AW DMCS Chromosorb W.
 - 10% Carbowax 20M/AW DMCS Chromosorb W.
 - 4% Carbowax 20M + 4% isophthalic acid/AW DMCS Chromosorb W.
 - 8% Carbowax 20M + 8% isophthalic acid/AW DMCS Chromosorb W.
 - 10% Versamid 900, /AW DMCS Chromosorb W.
 - 60-90 mesh Phasepak Q.

The recommended column gave the least solvent tailing and the best acrylamide peak shapes.

3. Other means of estimating peak areas were tried; only the recommended method gave a straight line calibration over the

the whole of the above range of acrylamide concentrations. Measurement of peak heights gave non-linear calibrations. Integration was not tried, but simple integration techniques would not be applicable to the lower quantities of acrylamide due to the sloping baseline created by the solvent tail.

4. Before injecting small quantities of acrylamide it was essential to check that the syringe did not contain residues of acrylamide from previous injections of larger quantities.
5. It was found that the calibration was stable for several days. However, it is recommended that it be checked every few injections.
6. In time the injection area of the column became fouled with non-volatile materials from extracts. This caused peak broadening and tailing. This could usually be cured by re-packing the first few inches of the column. If this was not successful a new column was prepared.
7. If solvents containing amounts of water greater than 20% were injected 'ghost' peaks could appear from previous injections. In these cases the solvent was repeatedly injected until the spurious peaks disappear.
8. Syringes were cleaned with water as well as the aqueous methanol to prevent their being jammed by deposits of polymer.
9. Standards deteriorated unless stored in the dark.

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by

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The use of polyelectrolytes in water treatment.

by
H.J. Boorsma
and
J. Hrubec

1. INTRODUCTION

The use of polyelectrolytes*⁾ in water treatment as flocculants and flocculation aids is based on a long tradition. In an initiative stage organic and inorganic polyelectrolytes of natural origin such as soluble starches, gelatins, tanins, alginates and activated silica have been used. Later the production of synthetic polymers has activated an increased application in water treatment processes.

Polyelectrolytes are used in water treatment processes for the following purposes:

- a) as coagulant for the destabilization of colloids and as coagulant aids for improvement of the floc characteristics (increased settling rate and floc strength) resulting in accelerated flocculation, improved floc stability, rapid sedimentation and improved water clarity;
- b) as filtration aid in order to promote filter operation at increased filtration rates with the same or even higher quality of the treated water;
- c) as a sludge thickening and conditioning aid to improve the dehydration and settling rates of solids from sludges in water treatment plants resulting in an improvement of the sludge filtrability.

Polyelectrolytes have been used with success when the traditional water treatment processes proved to be ineffective during the seasonal decrease of water temperature, in the case of an overloading of the treatment plant during rainfall and floods and in cases of the treatment of heavily polluted waters.

The most important limitation of a broader application of polyelectrolytes is the lack of a simple and reliable procedure for evaluating polyelectrolyte in laboratory tests before their application in full scale operation. In the same way, the lack of simple analytical methods for the determination of the residual concentrations and the possible high degree of toxicity of the synthetic polyelectrolytes are also limiting conditions of their use.

Regarding the use of polyelectrolytes for water treatment purposes in developing countries, there may be some additional complications due to instability of the majority of synthetic products under conditions of a prolonged storage period at the high air temperatures and high humidity of the tropical climates.

*⁾ The term "polyelectrolyte" is used in this study instead of term "coagulant aids" because the first term gives a more general description of the quality of these products.

The Scientific and Technical Committee of the International Water Supply Association is preparing a "Manual on Application of Flocculants for Potable Water Purification at Municipal Water Works". In the manual will be dealt with the technical problems of the polyelectrolyte application as far as handling and technology of application is concerned.

The problematical approach of the health hazards encountered regarding the usage of polyelectrolytes for drinking water treatment purposes is still in discussion.

2. THE NATURE AND CHEMICAL STRUCTURE OF POLYELECTROLYTES

Polyelectrolytes are generally water soluble polymers of organic or inorganic nature charged with ionised groups.

Originally the most frequently used inorganic polyelectrolyte in water treatment, was the so called activated silica.

Activated silica is considered to be a solution of polymeric silicates which are formed in the slow process of hydrolysis the partial neutralization of sodium silicate. The characteristic properties of the activated silica are determined by the initial conditions of preparation (initial silica concentration, reaction time, reaction pH and intensity of mixing) as a result of the difficulty of handling the technical complexity of dosing of the anorganic polymers. More and more priority is given to the use of organic polyelectrolytes because of the simplicity of preparation and dosing.

The organic polyelectrolytes are usually subdivided into three classes according to the electric charge of the Macro-ions which are dissociated in water: resp. nonionic polymers, anionic polymers and cationic polymers. Nonionic polymers can be prepared as polyalcohols, polyamides and poly(N-vinyl heterocyclics).

Anionic water soluble polymers can be synthesised from phosphonic, sulphonic or carboxylic acid substitution of long chain polymers. Cationic polymers can be prepared from the sulfonium or phosphonium substituted monomere compounds or by polymerization of ammonium substituted organics.

A substantial part of the polyelectrolytes used in water treatment processes are either of anionic or nonionic origin.

The structure of natural polyelectrolytes is mostly based on a polyalcoholic configuration corresponding with the natural cellulosic polymers.

The majority of the commercial synthetic nonionic and anionic polyelectrolyte products are based on polyacryl amide. Pure polyacrylamide is nonionic and prepared from the acrylamide monomer by polymerization. It is possible for example, to prepare nonionic acrylamides with molecular weights up to 10 million. The polyacrylamide can be subjected to a controlled hydrolysis which converts a part of the substituted carbon atoms to carboxylic groups. The resulting polymers will get an anionic character. The anionic acrylamide type polymers can also be prepared by the copolymerization of acrylamide and acrylic acid.

The nonionic and anionic polyelectrolytes are functioning as a coagulant aid, as such that they speed up the coagulation process, but they cannot replace the metal salts which are acting as the primary coagulants. It also appears that a minimum molecular weight of the polymer is necessary for a successful coagulation. The limited minimum molecular weight is also depending on such factors as the relative number of charged groups, the degree of branching of the polymeric structure, the charge of the colloidal particles and the ionic strength of the solution. The cationic polyelectrolytes are very promising of future application. Because positively charged polymers can act as well as destabilizing agents by bridge formation and as charge neutralization agents. A practical consequence of the ability of cationic polyelectrolytes to absorb specifically on negative colloids and neutralize the primary charge is that these materials do not require a large molecular weight to be effective in destabilization and they can be used in the absence of primary metal coagulants. Unfortunately the majority of cationic polyelectrolytes, with some exceptions, has a relatively high value of toxicity.

3. THEORY OF THE ACTION AND APPLICATION OF POLYELECTROLYTES

The most acceptable model for the explanation of the ability of polyelectrolytes to destabilize colloidal dispersion seems to be provided by the bridging theory.

According to the bridging theory, a polyelectrolyte must contain chemical groups which can interact with adsorption sites on the surface of the colloidal particle. When a polyelectrolyte molecule

comes into contact with a colloidal particle, some of the active groups are adsorbed at the particle surface. The pliable coiled threads remaining extended in the solution can attach other vacant adsorption sites of several colloidal particles. A particle-polyelectrolyte-particle complex is thus formed, in which the polyelectrolyte is serving as a bridge between the particles. Thus the optimum destabilization only occurs, when a small fraction of the available adsorption sites on the surface of the particles are covered and if the dosage of polyelectrolyte is sufficiently large to saturate the particle surface a restabilized colloid can be produced, since no sites are available for the formation of polyelectrolyte bridges.

On the basis of the bridging theory it can be explained that an effective destabilization and aggregation of colloids by polyelectrolyte dosing is often achieved with a polyelectrolyte having a similar charge as the particle. This theory is confirmed by the phenomenon that under certain conditions a system which has been destabilized and aggregated can be restabilized with extended agitation, giving rise to the breaking of particle-polyelectrolyte bonds.

The practical consequences of the bridging theory are involved to ensure an optimal average dosage of polyelectrolyte but also to prevent a localized overdosing by a rapid mixing and the addition of the polyelectrolytes in a too diluted solution. On the other hand a prolonged intensive stirring can break the floc aggregates.

4. TOXICITY OF POLYELECTROLYTES

From a public health viewpoint, in particular the toxicity of the synthetic polyelectrolytes is very important, because there is no doubt that natural polyelectrolyte such as activated silica, sodium alginate, starch products and cellulose derivations are in most cases non-toxic. From the synthetic polyelectrolytes anionic or nonionic products based on polyacrylamide, polyacrylic acid and acrylamide-acrylate and some types of cationic polyelectrolytes prevail in water treatment application and the greater part of toxicological studies were carried out with these products.

4.1 TOXICITY OF ANIONIC AND NONIONIC POLYELECTROLYTES

The toxicity of commercial products of polyacrylamide is caused by the residual presence of acrylamide monomer.

The toxicity of polyacrylamide is very low (6,7,8,9,10,11,21).

The acrylamide monomer may be present in the commercial products to the extent of a few percent. Williams (15) determines the acrylamide

concentration of 0 - 2.1 percent in some American commercial products. The majority of the toxicological tests was based on long term studies. In an investigation of the American Cyanamid Company (11) a polymer consisting of 90 percent acrylamide and 10 percent acrylic acid was fed to rats and dogs during a period of two years at dietary levels of 2.5, 5 and 10 percent for dogs.

No animals died as a result of this intake of polymer.

Throughout the two years feedtest with the polyacrylamides Seperan NP10, which is representative of the nonionic class of polyacrylamide and AP30 which is an anionic one, both containing a maximum of 0.08% monoacrylamide the laboratory test-animals (rats and dogs) tolerated 5-10% of these polyelectrolytes in their daily diet without harmful effects (10).

In agreement with this result, the investigations on the toxicity of the Russian product PAA (no data are available on the monomer concentration) also show a low toxicity of the polyelectrolyte (9).

LD₅₀ for white mice was fixed to be at a level of 12950 mg/kg day resp. 11250 mg/kg day for rabbits. From the results of chronic experiments during a period of 10 months, it was concluded that a dose of 1.5 mg/kg day can be considered as the threshold concentration for warm blooded mammals.

The relatively high toxicity of the acrylamide monomer was reported by Kuperman (13), Mc Collister (14). The LD₅₀ for rats, guinea pigs and rabbits ranged from 150 to 180 mg/kg day. Thrakhtman (9) gives the LD₅₀ for white mice and rabbits from 320.6 mg/kg day to 368 mg/kg day. Diagnostic signs of poisoning of the test animals resulting from excessive consumption of acrylamides should include stiffness and weakness in the hind legs, loss of ability to control the urinary retention, alaxia of front legs and inability of the animal to stand. These neurological effects can occur when sufficient high dosages are given either once or repeatedly, by any route of administration.

The cat was found to be the most sensitive species with a "no ill effect" dosage between 0.3 and 1.0 mg/kg day.

Mc Collister (14) concluded that if acrylamide, to which the general public will be exposed on a day-to-day basis, is applied, the total adsorption should not exceed 0.5 µg/kg day. This provides a large margin of safety (about 1000 fold).

4.2 TOXICITY OF CATIONIC POLYELECTROLYTES

One of the few cationic polyelectrolytes, which has been certificated by the U.S. Public Health Service Advisory Committee on Coagulant Aids in Water Treatment as safe for use in water treatment is Catfloc (1). Catfloc is a high molecular weight homopolymer of dimethyl diallyl ammonium chloride. Commercial Catfloc is a 15% aqueous solution of polymer solids. The polymer solids contain an average of 3% unpolymerized monomer.

However, the monomer is even less toxic than the polymer.

LD₅₀ of monomer is 5600 mg/kg day, LD₅₀ of polymer is 2800 mg/kg day (17). In the U.S.S.R. a toxicological investigation on the toxicity of cationic polyelectrolytes VA-2, VA-3, VA-2T, VA-3T has been carried out (20). VA-2 and VA-3 are products of ammonization of polystyrene by trimethylamine (VA-2) and by pyridine (VA-3). VA-2T and VA-3T are products of ammonization of polyvinyltoluene by trimethylamine (VA-2T) and by pyridine (VA-3T).

Long term feeding studies (7 and 10 months) of white mice, white rats and guinea pigs indicated that the VA-2 and VA-2T were the least toxic ones. The data of the chronic test proved that the VA-2 and VA-2T of the dose of 1 mg/kg day have a toxicological effect on the animals, at the dose of 0.1 mg/kg day this effect was temporal. At a dose of 0.02 mg/kg day no harmful effect could be established.

On the basis of these tests the VA-2 and V-2T products at a concentration of 0.5 mg/l have been approved (26) as the maximum permissible concentration in the water used for hygienic and domestic purposes.

5. REMOVAL OF POLYELECTROLYTES IN THE COURSE OF APPLIED WATER TREATMENT PROCESS

With regard to an evaluation of the toxicity hazards of polyelectrolytes applied in water treatment, the knowledge of data on the residual polyelectrolytes concentration after the flocculation process and the following treatment stages is important.

According to the published data the degree of polyelectrolyte polymers removal within water treatment is relatively high.

Sontheimer (18) mentioned the experience from a pilot water treatment plant at Leipheim, where the applied concentration of 0.3 mg/l polyacrylamide was decreased to 0.026 mg/l in the effluent of the coagulation clarifiers, finally to 0.01 - 0.002 mg/l in the effluent from the rapid sand filters and below 0.002 mg/l in the effluent after the activated coal filters.

Similar experience has been reported by Hässelbarth (3); a residual concentration of the polyacrylamide product Sedipur TF of 0.005 - 0.003 mg/l in the effluent of the coagulation unit, whereas no detectable concentration in the effluent of the rapid filter could be found. As far as the cationic polyelectrolytes are concerned, Black (19) reported that with appropriate coagulation the cationic polyelectrolyte could be removed to about 95 percent. From a viewpoint of safety, Packham (16) recommended to base the limit of allowable residual on the residual presence of the monomer instead of on the residual content of the polymer, because there is no reason to believe that the soluble monomer will be removed in the same degree as the polyacrylamide.

6. THE DETERMINATION OF POLYELECTROLYTE RESIDUALS

Up till now there is no simple, specific and sensitive method of determination of the residual concentration of synthetic polyelectrolytes in water.

Most attention has been given to the determination of residual traces of polyacrylamide in water and to the determination of the acrylamide monomer content in polymers (3,15,16,18,22,23).

The determination of the acrylamide monomer content in polyacrylamide products is mostly carried out by an extraction of the monomer from the products with a methanol-water mixture followed by an analysis of the extracts by UV spectrometry, by gas chromatography, by polarography or by bromination.

Regarding the methods of determination of the polyacrylamide in water, one of the most simple and sensitive methods is based on the measurement of the settling rate of a polyacrylamide solution by a standard kaolin suspension (3,18,22,25).

This method is suitable for the determination of 0.005 mg/l polyacrylamide. Packham (16) considered this method as not very convenient because of the interference by other coagulants, e.g. polynuclear complex ions.

7. RESULTS OF INTERNATIONAL INQUIRY

In 1970 the I.R.C. requested the Collaborating Institutions and other institutions in different countries for information with respect to the requirements or standards for polyelectrolytes application in water treatment, and on toxicological as well as on analytical procedures etc.

The resulting conclusions from this questionnaire which has been completed by 20 collaborating countries were as follows:

Synthetic polyelectrolytes are at present rarely used in developing countries.

There are no standardized analytical methods for the determination of residuals of polyelectrolytes in water nor for the analyses of polyelectrolyte trade products.

The standards for the application of polyelectrolytes are in the U.S.S.R. and in Czechoslovakia based on the permissible concentration of the residual of the polyelectrolyte in the water.

The Czechoslovak norm for the residual polyacrylamide product is fixed at 0.5 mg/l polyacrylamide whereas in the U.S.S.R. this norm is settled to the value of 2 mg/l. These standards are based on the information obtained from toxicological studies which have been performed by public toxicological agencies.

In the U.S.A. the Technical Advisory Committee on Coagulant Aids and in the U.K. the Committee on New Chemicals for Water Treatment approve individual polyelectrolyte products on the basis of information obtained from the toxicological research carried out by the manufacturers. The data on chemical composition, purity, uniformity, stability reaction properties, recommended levels of dosage, methods of application and in particular data on toxicity of products are required for an approval.

In U.K. the manufacturer must submit the technological scheme of production as one of the basic data for obtaining approval and in the case of changing the technology of production the products have to be re-approved.

For polyacrylamide products the Committee on New Chemicals for Water Treatment of the U.K. requires that the product must not contain more than 0.05 percent monomer and that the dose of the products

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For polyacrylamide products the Committee on New Chemicals for Water Treatment of the U.K. requires that the product must not contain more than 0.05 percent monomer and that the dose of the products

must not exceed 0.5 mg/l on average or 1 mg/l on any occasion. The U.K. "requirements" are conform to the recommendations of Mc Collister (14) that total adsorption of acrylamide should not exceed 0.5 μ g/kg day.

It seems justified to conclude that the U.K. system for approval of the use of a polyelectrolyte product in water treatment is the most practical and safe one.

SUMMARY AND CONCLUSIONS

A study of the application of polyelectrolytes in water treatment has been made. Most data were obtained from public agencies or manufacturers in USSR, USA, United Kingdom, and Czechoslovakia. The study has lead the authors to the following considerations:

A continued thorough examination of the actual and future knowledge of the toxological health hazards regarding the use of polyelectrolytes in water treatment is needed to ensure the fixation of an acceptable limit of allowance of toxic residuals.

Long term toxicological research is needed to confirm the proposed limits and the future use of the products.

Approval of the use of polyelectrolytes or chemicals in water treatment might preferably not be based on a limit of residual toxic components in drinking water, as it is difficult to determine the trace concentration of those in water. It might be advisable to base this approval on the maximum dose of the polyelectrolyte to be used in water treatment and on the maximum permissible concentration of the toxic components in the trade product.

Any approval or reapproval should be based on a reliable and standardized method of analyses.

For an assesment of the polyelectrolyte products, supplementary data on chemical composition, purity, uniformity, stability, reaction properties and methods of application are important. In the United Kingdom the manufacturers must submit a production scheme. In the case of changes in this scheme a reapproval of the product has to be requested.

For the execution of a policy of approval as described above, the set-up of national Committees of experts which should be charged with the previously draughted task is required.

In the Netherlands the I.R.C. has invited the Dutch Government to install a governmental Committee of experts for this purpose.

The National Committee is expected to draw up a list of those products to be used in water treatment practice, that the Committee consider subject to certain conditions to be unobjectionable on health grounds to the consumers involved.

A point of the discussion for the expert meeting could be to propose to WHO, to invite the national Governments to install national toxicological Committees to be charged with the approval of chemicals to be used in water treatment.

In a future stage WHO can be invited to coordinate the national efforts by setting up an international committee which can develop international standards of approval and recommendations of the WHO, resulting in a list of accepted and approved chemicals which can be distributed in the developing countries.

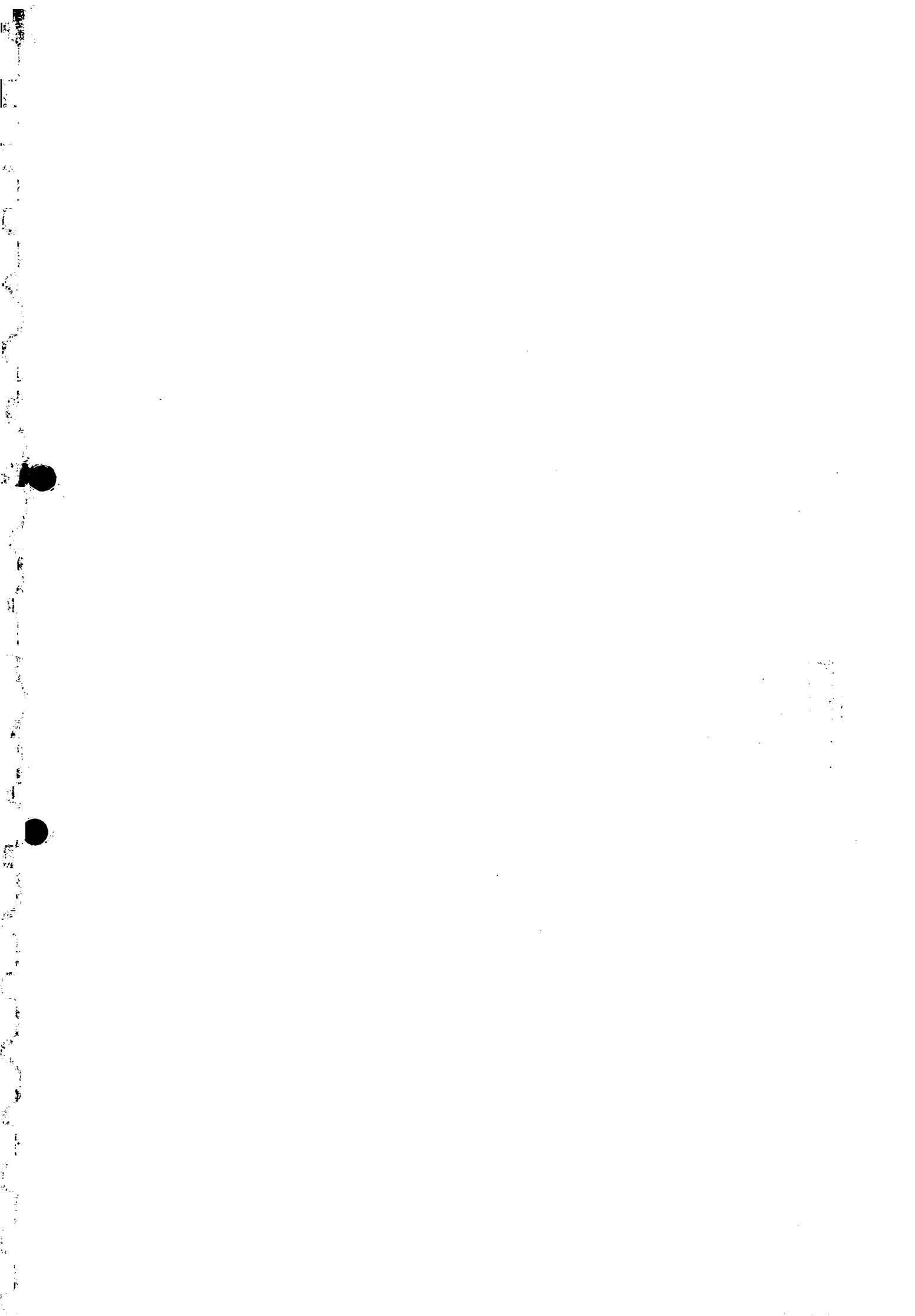
In the appendix of this report additional information has been made available with regard to the methods of analysis of acrylamide monomer with the consent of the Water Research Association.

The appendix also contains a photocopy of the Fifth Statement of the Committee on New Chemicals for Water Treatment in the United Kingdom. It may serve to elucidate the developed considerations.

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1. Introduction

Within the current WHO-programme of assistance as reported by the Director-General in the progress report for the twenty-fifth World Health assembly, contractual research projects are carried out concerning new water supply materials. Institutes in the United Kingdom and the Netherlands are investigating the process where stabilizers (such as lead) are leached from uPVC-pipe during conveyance of water.

As far as lead is concerned, the WHO Community Water Supply Unit have sponsored the Water Research Association (WRA), Medmenham, England and the Testing and Research institute of the Dutch Waterworks (KIWA), Rijswijk, the Netherlands. The WRA and KIWA have drawn up reports on lead levels in uPVC distribution systems and testing procedures for lead leaching from lead stabilized uPVC drinkingwater pipe (ref. 1, 2, 3 and 4).

The discussion paper deals with the current state of affairs on test methods, quality demands and field experiences for unplasticized polyvinylchloride drinkingwater pipe.

2. Use of unplasticized PVC for drinkingwater supply, historical background

2.1 Europe

Although in 1912 PVC production on a technical scale was made possible in Germany by direct reaction of hydrochloric acid and acetylene using catalysts, PVC pipe could not be manufactured before 1935, when problems of heat stabilisation and PVC quality were solved. In Germany the I.G. Farben Industrie installed on a experimental basis 400 drinkingwaterinstallations by using PVC pipe between 1936 - 1939 (ref. 5). The first DIN specifications were completed in 1941. After world war II contacts between plastic manufacturers and waterworksorganizations resulted in many experimental projects in which uPVC drinkingwater pipe have been used.

Until the second half of the fifties many problems such as cold brittleness, installation technicalities, joints and fittings had to be solved.

In the Netherlands the first draft test-specifications for uPVC drinkingwater pipe were completed in early 1954. This draft was approved in September 1956. The test specification included hygienic and toxicological demands concerning leaching of toxic materials from uPVC material.

This part of the test specification was used as a model for setting up several European test specifications such as in England, Norway, Belgium, Italy and was also used by ISO. In 1955 the Technical Committee 5 of the ISO installed the Subcommittee 6 which started their activities on standardization of uPVC pipe.

The Subcommittee 6 has been transformed into Technical Committee 138 in september 1970.

Since the end of the fifties the water supply has been a big market for uPVC pipe particularly for water mains and service pipes. Table 1 illustrates the use of uPVC drinkingwater pipe in the Netherlands, (mains and service pipes)

Table 1 - uPVC drinkingwater pipe in the Netherlands

Year	km installed
1962	2400
1963	2800
1964	3300
1965	3000
1966	2900
1967	2700
1968	2000
1969	2000
1970	1900
Total 1962-1970:	23000

2.2 United States

In 1954 the National Sanitation Foundation published a report called "A study of Plastic Pipe for potable Water Supplies", (ref. 6).

Twenty-two samples of plastic pipe including pipe extruded from PVC were involved in the study sponsored by the Society of Plastics industry.

After finishing this study a Public Health Advisory Committee (brought together by NSF) contacted the plastic industry leaders and outlined a programme for continuous testing and certifying plastic pipe for cold water service.

These tests are added to those related to the toxicological and organoleptic aspects of the pipe involving tests on toxicity, taste and odor and resistance of the pipe under conditions of use in practice. Products meeting the specifications are supplied by a NSF insignia.

According to the Plastics Pipe Institute the total plastic pipe Production in 1967 for water supply and distribution amounted to 123,000,000 pounds, being 36 % of the total plastic pipe production by end use. PVC, PE and ABS, in that order, are the major plastics used for pressure pipe for potable water service. An annual total plastic pipe production in the U.S. valued at \$ 350.000.000 for 1972 is predicted, meaning a doubling of the 1967 production within 5 years. Figure 1 illustrates the U.S. plastic pipe production from 1962 to 1967 (ref. 7).

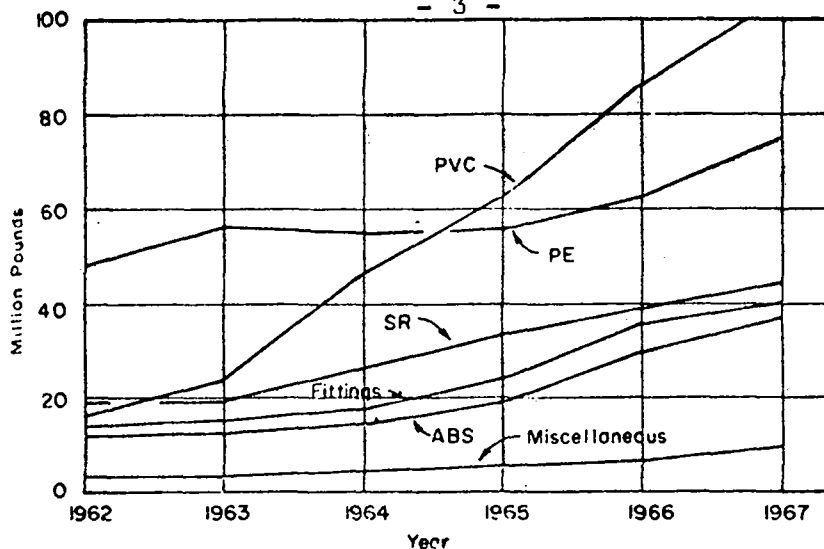


Figure 1

PLASTICS PIPE PRODUCTION BY MAJOR CATEGORIES

2.3 Outside Europe and the U.S.

As the potential market for sale of uPVC pipe is limited by shipping costs, uPVC pipe is usually manufactured locally, for Latin America mostly by U.S. owned or affiliated manufacturers (ref.7). In Asia some European owned manufacturers are operating.

3. Description of materials production and toxicological aspects

3.1 Materials and manufacture

Two types of polymerized vinylchloride are used for uPVC pipe production, i.e. emulsion PVC and suspension PVC.

For uPVC drinkingwater pipe in England, Germany and the Netherlands suspension PVC has nearly always been used. The advantages of the latter type of PVC are a higher purity, larger particle size so that single screw extruders can be used, and less water uptake. The suspension PVC may still contain small quantities of polymerisation catalysts such as inorganic mercury compounds, organic peroxides, Azo-compounds, persulfates and other products acting as redoxsystems, and water soluble suspension catalysts as organic colloids f.a. gelatin, pektin, polyacrylates, polymethacrylates, polyvinylalcohol and anorganic compounds as talcum, calcium phosphate and magnesiumphosphate.

uPVC pipe is made by extrusion of thermoplastic PVC using single or multiple screw extruders. Figure 2 illustrates a vented single screw extruder.(ref. 7).

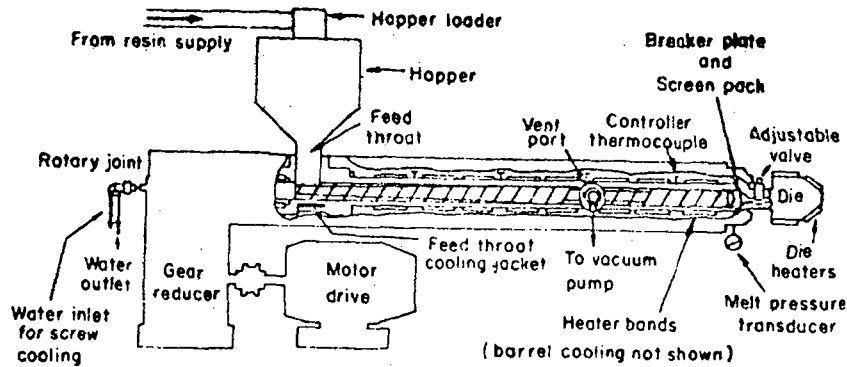


Figure 2
VENTED SINGLE SCREW EXTRUDER

Due to the high chloride content, PVC is unstable at temperatures exceeding 120°C . Because of thermoplastic deformation of the PVC temperatures between 150°C and 200°C are sufficient, heat stabilizers have to be added to the PVC material before entering the extruder. Besides heat stabilizers, lubricants are added to reduce internal and external friction during extrusion and light stabilizers and pigments are added to reduce PVC deterioration by UV radiation and to prevent growth of phytoplankton. Some manufactures use PVC granulate already containing the required additions.

In most European countries toxic lead compounds as lead stearate, di basic lead stearate, di basic lead sulfate are used as heat stabilizers and lubricants. Di basic lead phosphite acts as light and heat stabilizer. Lead stabilizers are not soluble in PVC. Non toxic compounds such as calcium stearate act as a lubricant and as a weak heat stabilizer. According to pipe manufactures the exclusive use of non toxic stabilizers for uPVC pipe production is unfortunately not yet possible with regard to the required mechanical properties of the uPVC pipe. Additions of the lead compounds already mentioned, sometimes in addition to products with synergistic action as barium - cadmium laurates are used. Quite a substantial proportion of organotin stabilizers are used in fittings. Barium-Cadmium compounds however are usually not allowed in food packing material but it is known that they are sometimes used for uPVC drinking-water pipe. It is clear that the use of toxic stabilizers for uPVC drinking-water pipe is only permissible when the leaching of the toxic compounds is restricted to an insignificant level considering the toxicological effects of the water quality. This includes:

- a. The quantity of toxic stabilizers or reaction products of stabilizers and hydrochloric acid, as a degradation product of PVC produced during extrusion, present on the surface of the pipe must be as low as possible.

These compounds give rise to an initial high lead or cadmium concentration in the drinking water during the period directly after installation.

- b. The toxic stabilizers must not be allowed to migrate to the surface area, for such migration will give rise to prolonged high levels of toxic materials in the drinking water.

In the U.S. no lead and cadmium compounds are used for uPVC drinking-water pipe production. In stead of these compounds tetra valenced organic tin compounds are used for heat and light stabilisation. Along with lead and cadmium compounds organotin compounds cannot be regarded as non toxic. The mechanism of degradation of uPVC at temperatures above 120 °C is the formation of hydrochloric acid from the decomposition of PVC at existing radicals. Hydrochloric acid itself does not act as a catalyst for further decomposition but according to Arlman (ref. 8) iron containing reaction products between hydrochloric acid and steel components from the extruder are stimulating the oxidation process by formation of new radicals.

3.2 Some notes on toxicity

3.2.1 PVC

The PVC material itself is not regarded as toxic as far as ingestion is concerned. However, only few experimental data are available. Animal feeding tests have been carried out by NSF using colonies of Wistar strain white rats which exclusively for 18 months drank water that had been in prolonged contact with PVC. The results of autopsies showed no evidence of any damaging actions finally attributable to the test chemicals (ref. 6).

Vinylchloride is a gas at temperatures above -13.8 °C its toxicity is relatively low. At concentrations over 500 ppm it has a slight toxic action and irritates the eyes. Vivylchloride is not soluble into water (ref. 9).

3.2.2 Lead

According to Patterson (ref. 10) the mean daily intake in the U.S. for lead amounts about to 440 µg per person, i.e. food 400 µg, air 30 µg, water 10 µg. Ten percent of the ingested lead is absorbed by the human body in so far water is concerned and 5% for food. Inhaled lead will rise to the extend of 50% depending upon particle size.

According to Kehoe (ref. 11, 12) a daily intake of lead of 600 μg during a lifetime may be considered as a safe limit. Prolonged higher quantities may lead to deleterious accumulation.

Kehoe observed deleterious effects of the daily intakes 1270 μg Pb after 8 years, 2350 μg after 4 years, 3270 μg after 8 months. There is no evidence that a slight increased intake of lead, during a short period can be regarded as a potential danger for public health.

The maximum acceptable load of lead from food and beverages has been tentatively fixed by the WHO at 0.005 mg per kg body weight per day. According to the second edition of the European Standards for drinking-water the upper limit of concentration for lead amounts to 0.1 mg per litre (ref. 13). In case of lead piping the lead-concentration should not exceed 0.3 mg per litre after 16 hours contact with the pipes. According to the third edition of the International Standards the upper limit for lead amounts to 0.1 mg per litre (ref. 14).

3.2.3 Cadmium

Cadmium is regarded as a strong accumulative toxic metal. Ingested cadmium is absorbed for a greater part by the digestive tract and from this part only a minor part is excreted by the body (ref. 15). It is clear that elevated cadmium levels must be avoided even for short periods. For this reason it should be considered to avoid the use of cadmium compounds in UPVC drinkingwater pipe. According to the second edition of the European Standards of the WHO the upper limit of concentration for cadmium in drinkingwater amounts to 0.01 mg per litre, which is in accordance with the third edition of the International Standards.

3.2.4. Mercury

Mercury is regarded as a high toxic accumulative metal. According to the WHO International Standards no acceptable daily intake for men can be estimated on the basis of the information at present available. The upper limit of concentration of 1 μg per litre, as given in the Standards, is related to levels found in natural water.

3.2.5 Barium

Barium salts are considered to be muscle stimulants especially for the heart muscle. By constricting blood-vessels barium may cause an increase in blood pressure. There is no evidence for its accumulation in bone, muscle, kidney or other tissue (ref. 25). A limit of 1 mg/l was established by FWPCA in 1968 (ref. 26).

3.2.6 Organo-tin compounds

The toxicity depends on the nature of the organic groups involved. In the ISO Draft proposal 5/6/3 N 218 "Permitted levels of lead and tin in uPVC pipes intended for the transport of potable water" and in BS 3505 a limit of 0.02 mg/l of dialkyl tin, C₄ and higher homologues has been set for the third extract (see page 9).

4. Existing test procedures

4.1 Introduction

Usually the test specifications include a general demand by which the PVC pipe is not allowed to contain ingredients in an amount which has been demonstrated to pollute the water in concentrations considered toxic. In contrast with plastic wrappings for food and foodproducts uPVC drinking-water-pipe is used for a long time and contact with chemicals is limited to drinkingwater. For uPVC waterpipe this includes that both the initial and the long term leaching of toxic substances into the water must be taken into consideration and that the toxicological consequences of leaching of toxic substances restricted to a short period direct after installation cannot be considered in an equal way as for wrappings. In Europe test specifications of uPVC drinkingwater-pipe include toxicologic and usually organoleptic demands. Toxicologic tests are mostly restricted to the leaching of toxic heavy metals using three successive extraction tests simulating the worst circumstances which may be expected in practice.

Maximum acceptable concentrations in the third extract should mostly be in accordance with approved maximum allowable concentrations of toxic substances in drinkingwater.

Most of the toxic heavy metals containing stabilizers used for stabilization of PVC are not insoluble in water and the uPVC material may very well contain up to 2 % in weight.

No specific tests are related to other non metallic organic additions which may be present in small quantities.

In the United States the National Sanitation Foundation published their Standards No. 14 for Thermoplastic materials, Pipes, Fittings, Traps and Joining materials. Its purpose is to establish the necessary public health and safety requirements for the above mentioned thermoplastic materials.

The differences among test specifications and demands especially between Europe and the U.S. have resulted in a different point of view concerning the acceptability of lead stabilizers for uPVC drinkingwater-pipes.

The N.S.F. is of the opinion that lead leaching from uPVC pipes gives rise to lead levels in drinkingwater which are not in accordance with the Public Health Service Drinkingwater Standards - 1962 (PHS Publication No. 956) and the WHO Standards.

The point of view in several European countries is that lead leaching from uPVC is only significant a short period directly after installation and the lead leaching decreases rapidly to insignificant low amounts.

Most of the European test specifications concerning leaching of toxic heavy metals are based on that philosophy.

Lead stabilized uPVC pipe of good quality can meet most European Standards but cannot meet the N.S.F. Standards, (see page 14). In the present situation lead stabilizers are used in Europe and organotin-stabilizers in the U.S.. For that reason the WHO Community Water Supply Unit has sponsored WRA and KIWA to investigate lead levels in uPVC distribution systems in the U.K. and in the Netherlands, specially with regards to the existing test specifications:

4.2 Toxicological and organoleptic aspects

Table 2 gives a survey of some methods for the determination of extractable lead in uPVC pipe.

The same extracts may be used for additional determinations such as other heavy metals present and organoleptic properties.

A review of some European and the NSF specifications for uPVC drinking-water pipe for cold water supply, in so far toxicity is involved, is given below:

England: British Standard 3505 : 1968 - Specification for unplasticized PVC pipe for cold water services.

Material

Chapter 2.1: "The material from which the pipe is produced shall consist substantially of polyvinylchloride, to which may be added only those additives that are needed to facilitate the manufacture of the polymer and the production of sound, durable pipe of good surface finish, mechanical strength and opacity.

TABLE 2

DETERMINATION OF EXTRACTABLE LEAD IN UPVC PIPE

Procedure specified	Pre-treatment	Extractant	Extraction period	Max. lead permitted	Notes
KIWA (Netherlands)	1 hr pre-washing with tap water at 3 m/min velocity rinse with distilled water.	150 mg/litre carbon dioxide in distilled water.	1. 48 hrs 2. 48 hrs 3. 48 hrs	1.0 mg/litre 1.0 mg/litre 0.3 mg/litre	Take arithmetic mean of results on 3 specimens. Extract at room temperature.
B.S.I. (UK)	6 hrs pre-washing with tap water at 3 m/min velocity. Rinse with distilled water.	150 mg/litre carbon dioxide in distilled water.	1. 48 hrs 2. 48 hrs 3. 48 hrs	1.0 mg/litre - 0.3 mg/litre	Take arithmetic mean of results on 3 specimens. Extract at room temperature.
Germany	1 hr pre-washing with tap water at 3 m/min velocity (diam. 30 mm) 2 hrs diam. 30 mm	0,01 N sodium bicarbonate	1. 48 hrs 2. 120 hrs 3. 240 hrs	900 µg/litre 2250 µg/litre 500 µg/litre	
I.S.O. (International Organization for Standardization) ISO Draftproposal	1 to 6 hrs pre-washing with water at 3 m/min velocity. Rinse with distilled water.	150 mg/litre carbon dioxide in distilled water.	1. 48 hrs 2. 48 hrs 3. 48 hrs	1.0 mg/litre - 0.3 mg/litre	Take arithmetic mean of results on 3 specimens. Extract at 20 ° ± 5 °C.
N.S.F. (U.S.A.)	Pieces of UPVC 600 cm ² surface area per 400 ml extractant	Ann Arbor water carbon dioxide pH 5.0	72 hrs	≤ 0.05 mg/litre	10 inversions, 3 times each 24 hours extract 100 °F (37,8 °C)

None of these additives shall be used separately or together in quantities sufficient to constitute a toxic hazard, or to impair the fabrication or welding properties of the pipe or to impair its chemical and physical properties as defined in this standard."

Sampling

Appendix E2: "For the purpose of this test the pipes shall be grouped according to their method of manufacture and the type of extrusion compound used. Test specimens shall be taken at least once per year from the smallest size pipe within each group, and all specimens shall meet the requirements given in 8.6. Whenever a change in the method of manufacture or in the extrusion compound leads to the establishment of a new group, test specimens shall be taken from the smallest sized pipe within the new group and these shall meet the requirements given in 8.6 before the pipes are taken into stock."

Physical and chemical characteristics

Chapter 8.6 Effect on water.

"The pipes shall not have any detrimental effect on the composition of the water flowing through them.

When tested by the method described in Appendix E the quantities of lead and dialkyl tin C₄ and higher homologues (measured as tin) and any other toxic substances extracted from internal walls of the pipe shall not exceed the following concentrations in the test solution:

lead (1st extraction) ≤ 1.0 mg/l

lead (3rd extraction) ≤ 0.3 mg/l

Dialkyl tin C₄ and higher homologues ≤ 0.02 mg/l.

Other toxic substances ≤ 0.01 mg/l.

When so required by the purchaser, the manufacturer, for the purpose of these tests, shall disclose the main toxic substances present.

Note: Conformity with the requirements of this clause will ensure that the recommendations of the WHO 1963 concerning toxic contaminants of drinkingwater are not exceeded."

No characteristics for taste, odor and colour are included.

Marking Chapter 11.

11.1 "All pipes shall be indelibly marked at intervals no greater than 3 m. The marking shall show the following in the order stated:

- (1) The manufacture's identification
- (2) The number of this British Standard i.e. BS 3505
- (3) The nominal size, as shown in Table 1, and class.

Adhesive labels alone shall not suffice.

11.2 The marking shall be imprinted longitudinally in the following colours in accordance with BS 4159

Class B, red Class D, green

Class C, blue Class E, brown

It is strongly recommended that use is made of the same operated by the British Standard Institution where by the product may bear the registered mark of the BSI.

Test methods directed to the effect on water

See table 2

Germany: - DIN 8061 - Rohre aus PVC hart, erhöht schlagzähe, Allgemeine Güteanforderungen - Prüfung
- DVGW Arbeitsblatt 320 - Verwendung von Kunststoffrohren in der Trinkwasserversorgung
- Mitteilung aus dem Bundesgesundheitsamt, Gesundheitliche Beurteilung im Rahmen des Lebensmittelgesetzes II
Mitteilung XIX. Trinkwasserversorgungsrohre aus Kunststoffen.

Material

DIN 8061 chapter 2.1: "Modified PVC without plasticizers have to be used. The choice of stabilizers etc. are due to the manufacturers with the restriction that uPVC pipe has to meet the DVGW Arbeitsblatt and the quality demands of the Bundesgesundheitsamt."

DVGW Arbeitsblatt W 320: "Products of unknown composition and rework material are not allowed to be used."

According to th 11. Mitteilung aus dem Bundesgesundheitsamt uPVC drinking-water pipe is safe for conveyance of drinkingwater in case the material meets the prescribed composition.

Two-basic lead-stearate; two basic lead sulfat, two basic lead sulfat and two basic lead phosphite may be used totalling till 2 % in weight for lead as a maximum.

Sampling

DVGW Arbeitsblatt W 320 item 2.1.12 : "One time per year as a minimum and in case of a change in the extrusion compound (minimum nominal size of pipe 40 mm).

Physical and chemical characteristics

DVGW Arbeitsblatt W 320 chapter 2.1.12: " uPVC pipe and fittings are not allowed to produce taste, odor and colour, nor may leach toxic substances in concentrations toxic for man. Bacterial growth and growth of algae may not be stimulated.

In addition uPVC pipe has to fulfill the requirements by the Bundesgesundheitsamt,

Marking

DVGW Arbeitsblatt W 320: "The pipes have to be marked at distances of about 1 meter with DIN mark, name of manufacturer, number of extruder, code number concerning the composition of material, diameter and maximum working pressure.

Test methods directed to the effect on water

See table 2

The Netherlands: KIWA keuringseisen nr. 49 - Waterleidingen van ongeplasticeerd polyvinylchloride (1972)

Material

Chapter 1.2: "The material from which the pipe is produced shall consist of unplasticized polyvinylchloride to which may be added only those additives which are needed to facilitate the manufacture of the polymer, and the production of the pipe. Pigments may be added."

Sampling

Chapter 1.4: "For the purpose of the test the pipes must be at least 15 hours of age."

Physical and chemical characteristics

Chapter 2.6 Effect on water: "The pipes shall not have any detrimental effect on the composition of the water flowing through them. The pipes are not allowed to produce taste, odor and colour and may not leach toxic substances in concentrations toxic for man.

Chapter 2.6.1 Leaching of toxic substances: " When tested by the methods as described in 2.6.1 (see table 2) the quantities of lead, arsene, cadmium, chromium, tin and mercury shall not exceed the following concentrations in the test solution:

Lead (1 st extraction) \leq 1.0 mg/l
(2 nd extraction) \leq 1.0 mg/l
(3 rd extraction) \leq 0.3 mg/l
Arsene; cadmium, chromium, tin and mercury \leq 0.05 mg/l
Other toxic substances \leq 0.05 mg/l

Chapter 2.6.2 Taste and odor:

1 st extraction: with a delution of 1 : 10 no taste or odor
may be present

Chapter 2.6.3 Increase in colour:

3 rd extraction: \leq 5 mg Pt/l.

Marking

Chapter 2.10: "The pipes have to be continuously marked with name of manufactures or trade name (marque dépos ) - KIWA - PVC - pressure class - nominal diameter x wall thickness (in mm) - productionperiod - number of extruder, the last two dates may be in code.

Test methods directed to the effect on water

See table 2

ISO: TC 5/SC 6 Draft proposal 318 - Extractability of lead and tin of uPVC pipes (test method) and TC 5/SC 6 Draft proposal 296 - Permitted levels of lead and tin in uPVC pipes intended for the transport of potable water. The draft proposals are only related to the extractability of two types of stabilizers i.c.

1. lead salts of organic acids
 2. organic derivates of tin, mainly dialkyltin C₄ and higher homologues.
- See for test methods table 2.

When tested by the ISO method the quantities of lead and tin shall not exceed the following concentrations in the test solution:

lead (1 st extraction): \leq 1.0 mg/l
(3 rd extraction): \leq 0.3 mg/l
tin (3 rd extraction): \leq 0.02 mg/l

Remark: The draft proposals are subject to revision and they are expected to be published soon as Draft International Standard.

United States of America: - National Sanitation Foundation standard number 14 and "A study of plastic pipe for potable Water Supply" published by the N.S.F. (1955).

Material

NSF Standard number 14, section 3, item 3.00 General:

"Materials used in manufacture of pipe, fittings, valves, traps, joining materials and appurtenances covered by this Standard shall meet the public health and safety as well as performance requirements as established here in for the intended use or application. All such materials shall be manufactured in a manner which will prevent introduction of possible contamination thereto. Item 3.001 Such quality procedures and reports are deemed necessary to continued uniform quality of the materials and continued compliance with the applicable ASTM requirements for said material may be required.

Item 3.002 "The addition of innocuous tracers to materials covered by this Standard may be required when so recommended by the NSF Joint Committee on Plastics."

Item 3.003 "The manufacturer shall submit, at the time of requesting evaluation and qualification of a thermoplastic material and/or joining material, complete information for such material. When any change is made in the formule or in the source of supply of ingredients therein, such additional information shall also be submitted.

Said information shall be retained on a confidential basis."

Item 3.02 "Potable water application: Thermoplastic materials for pipe, fittings, valves, joining materials and/or appurtenances for potable water applications shall contain no ingredients in an amount which has been demonstrated to migrate into water in quantities which are considered toxic and shall conform to the specific requirements as stated in item 3.021 Toxicological and organoleptic - and 3.022 - Physical requirements.

Physical and chemical characteristics effect on water

NSF Standard number 14, section 4 - Requirements for pipe, fittings, valves and traps, item 4.01 - Toxicological and organoleptic requirements.

"Thermoplastic pipe, fittings, valves and appurtenances, intended for potable water application shall conform to the toxicological and organoleptic requirements in items 3.02, 3.021 and 3.022."

Item 3.02 - Potable water application: see Material.

Item 3.021 - Toxicological and organoleptic: "The toxicological and organoleptic evaluations of the analyses specified in Appendix B shall meet the minimum public health requirements.

Item 3.022 Physical requirements: Thermoplastic materials shall comply with the physical, chemical and performance requisites of the latest applicable Standard(s) of the American National Standards Institute (ANSI); American Society of Testing Materials (ASTM); or the Commodity Standards Division of the U.S. Department of Commerce (CS); as determined by the NSF Joint Committee on Plastics.

Sampling

Policy B includes a Statement of policy relating to sample collection - testing - reporting - samples required.

Item 1: "Actual laboratory examination of specimens of materials offered for use in the extrusion of plastic pipe is required and actual laboratory examination of specimens of extruded plastic pipe also is required before the right to use the NSF Seal of Approval on such materials and pipe is initially granted and at least once a year thereafter."

Item 2: "Actual laboratory examination of specimens of materials offered for use in the extrusion of plastic pipe is required and actual laboratory examination of specimens of extruded plastic pipe also is required before the right to use NSF Seal of Approval on such material and pipe is initially granted, and at least once a year thereafter."

Marking

An NSF Seal of Approval is applied on uPVC pipe meeting the NSF standard number 14. The material is "listed" by the NSF.

Section 4 - Requirements for pipe, fittings, valves and traps - item 4.03: Marking and coding of pipe, fittings and traps, and appurtenances:

"The manufacturer shall place on all thermoplastic pipe, fittings, valves and traps, and appurtenances, the designations and identification required in the latest applicable ANSI, ASTM or CS Standard(s) as determined by the NSF Joint Committee on Plastics. Provided, however that fittings and valves of such size and/or configuration as to preclude use of the complete marking shall be at least identified as to the manufacturer and type of material."

4.031 "All required markings shall be legible and so applied as to remain legible under normal handling and installation practices."

4.032 Thermoplastic pipe, in addition to the above, shall bear an appropriate code which will assure identification on the pipe as to the month of production and resin formulas used in the production of said pipe.

Manufacturer shall maintain such additional records as are necessary to confirm identification of all pipe so coded.

Such records shall be made available to the laboratory upon request. The following indicates the required markings and code information.

Pipe size	Type material	Pressure PSI	Commercial Std.No.	Trade name	Code	NSF logo
2"	PVC 1120	200 psi	CS 250-63	ICY	1510A	n Sf

Test methods

See table 2 and "A study of plastic pipe for potable water Supplies" published by NSF (1955).

According to section 4 item 4.05 the NSF Standard nr. 14 - Special test requirements- : Special tests may be required on thermoplastic pipe, fittings, valves, traps and appurtenances when recommended by the NSF Joint Committee on Plastics, when deemed necessary to assure adequate protection of the public's health and safety.

France: NF T 54-003 (July 1972) - Matières Plastiques - Tubes en polychlorure de vinyle non plastifié - Spécifications Générales.

NF T 54-016 (July 1972) - Matières Plastiques - Tubes en polychlorure de vinyle non plastifié pour la conduite et la distribution de l'eau avec pression - Spécifications.

NF T 54-017 (July 1972) - Matières Plastiques - Tubes en polychlorure de vinyle non plastifié pour installations sanitaires - Spécifications.

NF T 54-019 (May 1969) - Matières Plastiques - Tubes en polychlorure de vinyle non plastifié pour la conduite de liquides alimentaires - Spécifications.

Material:

No restrictions to the composition of the PVC material are included.

Sampling

NF T 54-003, item 5 includes general prescriptions.

Physical and chemical characteristics, effect on water

NF 54-003 - General aspects, item 14:

"A partir des caractéristiques générales données par la présente norme, qui sont les caractéristiques de base de polychlorure de vinyle non plastifié mis sous forme de tube, sont établies des normes particulières pour les différentes utilisations possible. Elles désignent, par leurs dimensions nominales, les tubes choisis pour l'application considérée compte tenu:

- du régime d'écoulement, avec ou sans pression;
- de la résistance à la corrosion ou l'abrasion par les fluides véhiculés;
- de la température d'utilisation;
- de la situation et des conditions d'établissement de la canalisation.

Elles fixent dans chaque cas, les caractéristiques particulières de ces tubes: mécaniques, physiques, physico-chémiques, toxicologiques etc.."

NF 54-016, -017, -019 item 3.2.4 - Solubility, taste, toxicological characteristics: "uPVC pipe have to be in accordance with general prescriptions on materials which may be in contact with food and beverages".

The pipes may neither leach any substance nor produce any taste and colour. However, no test methods and maximum acceptable levels have been included.

For transport of mineral water an additional approval by the ministre "de la Santé Publique" is required.

Marking

NF T 54-003 item 2.2: "Un tube conforme à la présente norme doit porter un marquage constitué par:

- la marque du fabricant ou un signe permettant d'identifier celui-ci;
- la symbole de la matière qui la constitue: PVC;
- éventuellement, les indications prévues par les normes particulières;
- ses dimensions nominales, diamètre extérieur et épaisseur, séparés par le signe X.

Item 2.3 Colour: "la couleur doit être:

- gris foncé lorsqu'il est destiné à la conduite de liquides alimentaires;
- gris clair lorsqu'il n'est pas destiné à la conduite de liquides alimentaires.

Test methods directed to the effect on water

No test methods are included. According to the standards, test methods may be set up individually up till now.

A draft test method nr. T 54-027 on leaching of lead and tin has been set up recently.

4.3 Discussion

In so far the toxicity of uPVC pipe is concerned the specifications mentioned above in principle are based on a number of common points of view.

1. All specifications described include a general demand on the composition of the material such as: "The material shall contain no ingredients in an amount which has been demonstrated to migrate into water in quantities which are considered toxic. The water which has been in contact with the plastic material have to meet official quality standards.
2. Additions may only be utilized when required to realise the polymerisation process and to make possible the extrusion of uPVC pipe. Innocuous tracers to materials may be used in so far the specifications can be met.
3. Complete information on the composition of the material used for production shall be submitted by the manufacturer to the purchaser on request before uPVC pipe can be tested according existing specifications.
4. Based on the informations of the manufacturer, tests on toxicity are commonly restricted to the leaching of a restricted number of heavy metals which are known to be present in the uPVC. Sometimes organoleptic properties are included.

The NSF also includes materials such as compounders delivered by material suppliers.

5. Changes in the composition of raw materials commonly include new testing of the uPVC pipe produced. Commonly the manufacturer is obliged to submit data to the testing institute on beforehand.
6. Normal frequency of testing on toxicity amounts to 1 time per year.
7. Basic data have to be marked on the outside of the uPVC drinkingwater pipe including the seal of approval.
8. The test methods for the determination of the leaching of toxic materials are mainly based on extraction test simulating the worst conditions to be expected in normal practice.
9. The French standards do not prohibit the use of toxic stabilizers however, no leaching of any substance from uPVC drinkingwater pipe is allowed.

It is not yet clear how such an absolute demand functions in practice as no test methods for the leaching of substances are described. According to the Standards, test methods may be set up individually.

Concerning the leaching of lead and tin from uPVC drinkingwater pipe a draft test method nr. T 54-027 has been set up recently.

5. Lead levels in uPVC distribution systems

5.1 Introduction

There is an evidence that pipes complying with the standards relating to the use of lead stabilizers in uPVC will not produce high concentrations of lead in drinking water.

- In 1959, Boelens (ref. 16) examined water samples from 24 uPVC mains in the supply area of the Waterworks Overijssel before and after a period of standing of the water in the pipe, ranging from a few hours to 9 months. The period that the pipe had been in service ranged from 2 months to 5.5 years. Sixty tests have been made and only two samples contained a lead concentration greater than 0.05 mg/l after a period of standing that lasted 4 months and some days. The lead concentrations respectively amounted to 0.07 mg/l and 0.10 mg/l. The nominal diameters of the pipes ranged from 15 - 100 mm.
- In 1961 the "Bundesgesundheitsamt Berlin" carried out a similar survey in some other parts of the supply area of the same waterwork (ref. 17). Water samples have been taken from ten uPVC mains before and after a period of standing. Out of 20 samples the lead content of one sample passed 0.05 mg/l after a standing period. The lead concentration amounted to 0.09 mg/l after a standing period of 12 hours.
- The KIWA committee on Plastic Water Pipes took water samples from 11 uPVC water mains at three different times after standing periods from 12-24 hours (ref. 18). The mains were located in various places throughout the Netherlands. From 33 water samples, 14 proved to have lead contents which exceeded 0.05 mg/l after periods of standing. None of the samples exceeded the Dutch standard of 0.3 mg/l of lead after standing for 16 hours (ref. 19).
- Everard reports experiments in which hard water was allowed to stand in uPVC pipes manufactured to B.S, 3505 for periods ranging from 22 hours to 28 weeks (ref. 20). The lead contents of the water after these periods of standing was reported as 0.1 mg/l in nearly all cases.
- Visintin and Monteriolo (ref. 21) examined water samples from Italian uPVC mains of length varying from 250 m to 4 km. The lead contents of the uPVC from which these pipes were made varied between 0.031 - 1.619% and the pipes had been in service for periods ranging from a few weeks to three years. It was found that the concentration of lead was less than 0.07 mg/l in 31 out of 32 pipes. A concentration

as high as 0.09 mg/l was found only in a new 4 km main. After three years service the lead content of the water in the same pipe was at the extent of 0.01 mg/l.

— Cosoveanu (ref. 22) carried out series of tests on uPVC pipe of Rumanian manufacture and showed too that the quantity of lead, extracted by water from a new pipe, decreased rapidly.

— Tests conducted in Peru (Bracale, Chuy) in 1967 lead to these conclusions (Private communication):

1. The concentration of lead in the extracting water is extremely low for PVC pipe stabilized with lead and is much lower than is permitted by the standards for potable water.
2. The quantity of lead decreases in time, after being proved experimentally in the laboratory and by analysis of samples, taken from the distribution systems so that the total amount of the extractable lead is depleted in a no greater period than 90 days.
3. It is considered that these pipes under normal service conditions offer no risk for the health of the users of potable water systems. (Peru specifies that only calcium and zinc may be used as stabilizers for drinking water pipes).

From the information obtained it can be concluded that there is no evidence that the upper limit of concentration for lead in drinkingwater (0.10 mg/l) as recommended by the WHO (ref. 13,14) is exceeded even after periods of standing. On request of the WHO the Water Research Association and KIWA have recently carried out an investigation of lead levels in uPVC distribution systems in the U.K. and the Netherlands. The WRA involved water mains of \geq 25 mm nominal bore. The work of KIWA is mainly related to small bore uPVC drinkingwater pipes in distribution systems in the Netherlands. The pipes are in accordance with the KIWA specification nr. 49 and BS 3505.

5.2 Lead levels in uPVC distribution systems in the U.K. (ref. 2)

The sampling programme was designed to cover as many different situations as possible. Distribution systems were therefore surveyed to supply water, covering a range of compositions. Samples from old and new pipes of various sizes and manufactures were obtained from where ever possible. Many pipes were sampled under both normal and night flow conditions.

Of 77 samples examined 37 were found to have a lead concentration 0.01 mg/l or less and none exceeded 0.05 mg/l.

In addition to the general survey a newly installed pipe was sampled during a period of 32 days to determine the trend of lead levels.

Table 3 give the results.

Table 3 lead concentration in water from a new 25 mm nominal bore uPVC service pipe.

Length of pipe prior to sampling point 6.1 m. Manufacturer S. Water Analysis 0.

Period in service days	Total volume of water passed m ³	Static sample		Flowing sample. Lead content mg/l
		Standing period hours	Lead content mg/l	
0	0	14	0.11	0.01
1	0.83	14	0.03	0.06
4	1.64	62	0.09	0.02
5	2.46	14	0.02	0.02
6	3.26	14	0.01	0.02
7	4.10	14	0.02	0.01
8	4.91	14	0.01	0.01
11	5.74	62	0.02	0.01
12	6.54	14	0.06	0.01
13	7.38	14	0.02	0.01
14	8.30	14	0.02	0.02
15	9.00	14	0.02	0.01
18	9.85	62	0.02	0.01
29	17.2	14	0.01	0.02
32	18.2	62	0.01	—

5.3 Lead concentrations in uPVC distribution systems in the Netherlands (ref. 4)

In 1969 water samples were collected from water mains and connected uPVC service pipes. The water quality concerned includes the greatest possible differences occurring in the Netherlands.

In total 11 of the 18 mains were made of uPVC, 4 asbestos cement and 3 cast iron. In 9 of the 18 water samples no lead could be detected (less than 0.001 mg/l), in one uPVC water main the lead level increased 0.05 mg/l (0.055 mg/l) as laid down by the former WHO International Standards.

The water appeared to be contaminated with ferric hydroxide flakes so that adsorption of lead may have been occurred. Water samples taken from a connected uPVC water pipe did not contain any measurable lead in normal flowing conditions.

Flowing samples were taken from 22 uPVC service pipes. The lengths varied from 4 to 452 meters, the oldest pipe was laid in September 1955, the newest had only been in service for 1 month. The nominal bore varied from 16 to 50 mm. Lead levels appeared to be < 0.01 mg/l.

In total 25 uPVC service pipes were sampled after periods of standing which ranged from 10 minutes to 114 days. For 10 of the 25 samples, the lead concentration in the water at the end of the standing period amounted to < 0.001 mg/l; for 8 samples 0.01 mg/l; for one sample 0.015 mg/l, for one sample 0.03 mg/l, for one sample 0.04 mg/l and for one sample the exceptionally high value of 0.6 mg/l.

The standing period in the last uPVC pipe amounted to 84 days. After flushing the uPVC pipe with a quantity of water equal to two times the content the lead concentration amounted to 0.01 mg/l.

Besides of the field survey the initial lead leaching of 8 different uPVC pipes of 4 different makes were studied using drinking water of the Hague. The nominal bores amounted to 16 and 25 mm. Graphs one and two give the results. It can be seen that the main lead leaching during flow is restricted to the first 30 minutes and that the highest lead concentrations occur in the pipes with the smallest diameter.

From the work of KIWA can be concluded that with exception of one high value of 0.6 mg/l, the average increase of the lead concentration in the drinking water after standing periods in uPVC pipes is 0.004 mg/l. Under conditions of flow the average decrease in the lead content in the water is 0.001 mg/l.

Both WRA and KIWA concluded that lead concentrations in water sampled from uPVC distribution systems were in general very low and in most cases were almost identical to the lead content of the water before coming into contact with uPVC. There is no evidence therefore that the use of lead stabilizers in uPVC pipe manufactured according to B.S. 3505 and the KIWA test specifications nr. 49, constitutes a long term health hazard to the domestic water consumer.

Tests on newly-installed pipes showed that these pipes can give rise to lead concentrations higher than 0.05 mg/l initially, but these fall to acceptable levels within a few days or weeks.

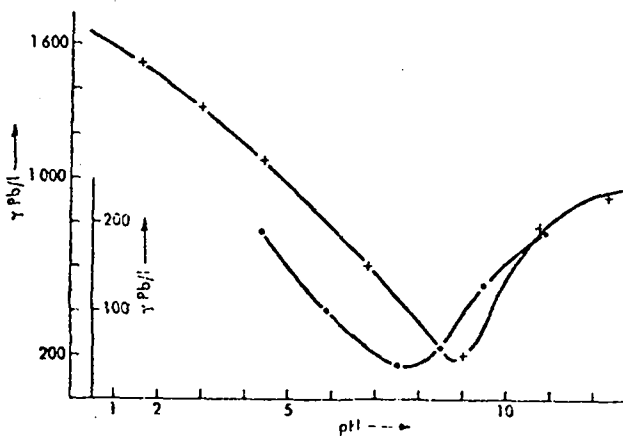
5.4 Some quality aspects affecting lead levels in uPVC drinking water pipe

As drinking water normally has been treated in Europe no big changes in water quality may be expected. In practice lead leaching from uPVC pipe appears to be very low and no effect of the water quality on lead levels could be determined.

Effect of acidity and temperature

Sontheimer and Wagner (ref. 23) studied the effect of acidity temperature and sodiumchloride on lead leaching from new uPVC pipes. Graphs 3 and 4 show the effects of pH and temperature.

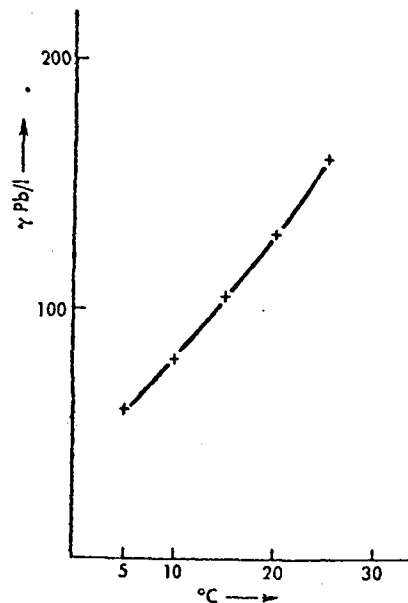
Graph 3



The effect of pH on lead leaching, standing period: 24 hours

- x— without pre-treatment
- after 5 extractions with 0.01 M NaHCO₃

Graph 4



The effect of temperature on lead leaching, standing period: 24 hours

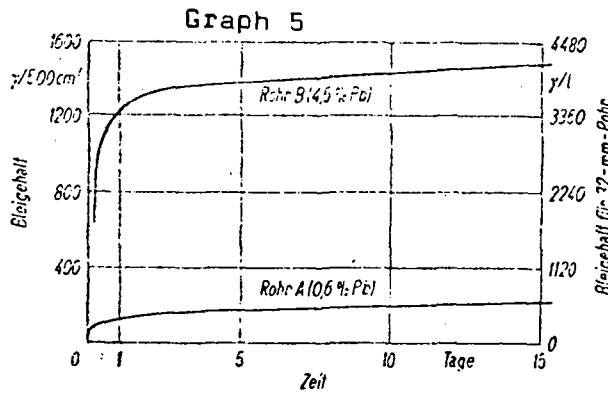
(extractant: 0.01 M NaHCO₃)

Effect of sodium chloride

Sodiumchloride did not effect the lead leaching between 5 and 100 m Mol/l.

Effect of lead content in uPVC

Niklas and Meijer (ref. 24) studied the effect of the lead content of new uPVC material on lead levels in drinking water. Standing periods lasted 15 days at a temperature of 20°C. Graph 5 gives the results. It can be concluded that lead levels were about seven times higher using uPVC pipe with 4,5 % lead in weight in comparison with a pipe containing 0.6% lead.

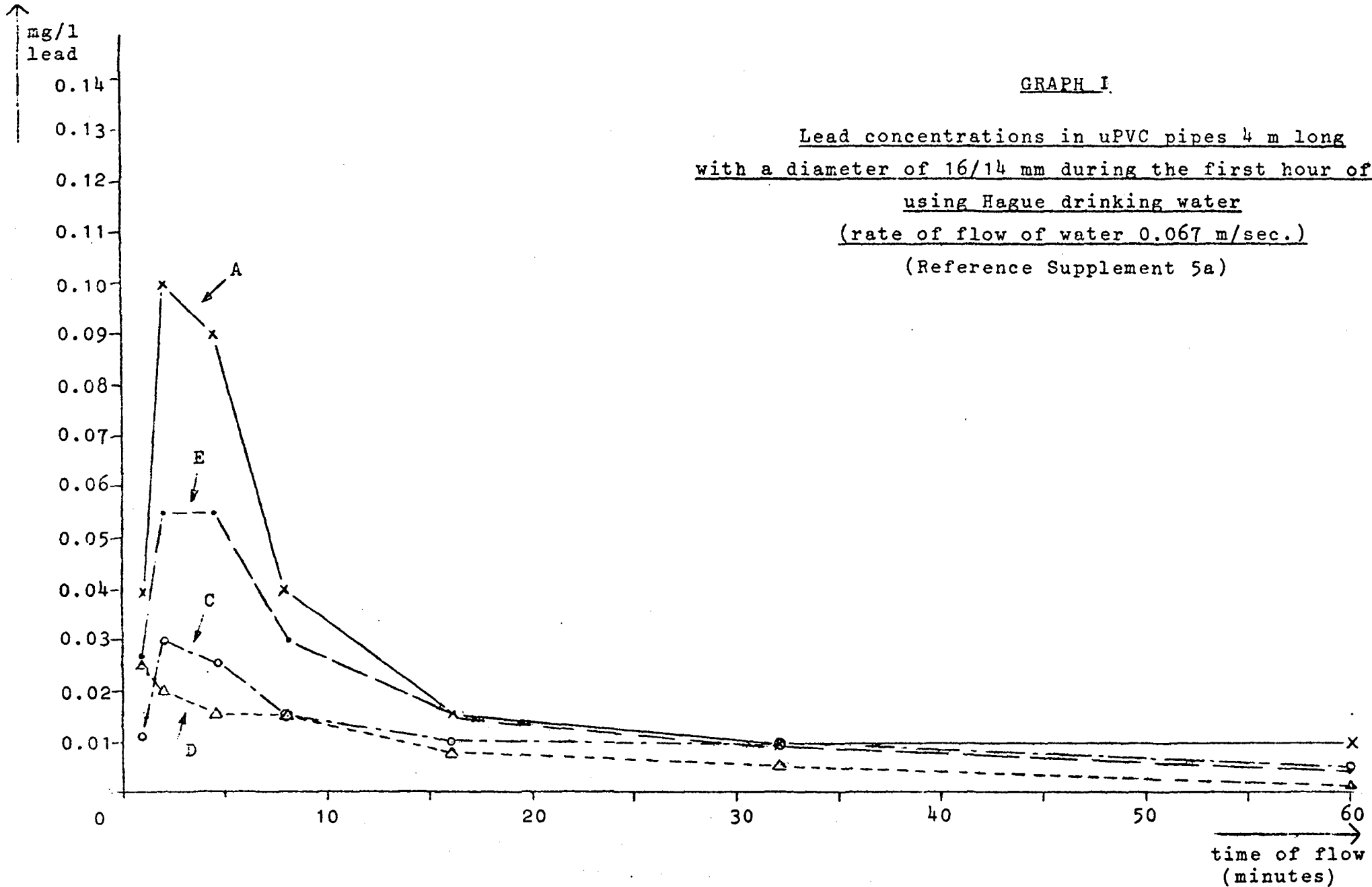


Effect of polyphosphates

The effect of sodiumhexametaphosphate on the extraction of lead from uPVC pipe was investigated by the WRA. It was found that the presence of 5 mg/l of sodiumhexametaphosphate more than doubled the amount of lead extracted initially from new pipe with water. On a sample of pipe that had been in service for 9 months the effect was very small of negligible.

6. Some special tests concerning test methods

The results of the survey of lead concentrations in uPVC distribution systems have proved that the existing tests based on the I.S.O. type have reassured that no long term health hazard due to the use of lead stabilizers in pipes meeting the standards was indicated. The potential hazard was essentially short term in nature and could not realistically be assessed in relation to the WHO standards for drinking water in which the levels, set for toxic substances, were based on exposure to the toxic substance during a lifetime. According to Packham of the WRA a test of shorter duration, with a stable extractant and involving a degree of agitation would have advantages especially in terms of convenience over the procedures of the ISO type (ref. 1 and 3). Packham states that it is questionable, however, whether an arbitrary test is a satisfactory basis for a standard. The test as it stands provides a measure of the level of extraction at some indefinite time in the life of a pipe.

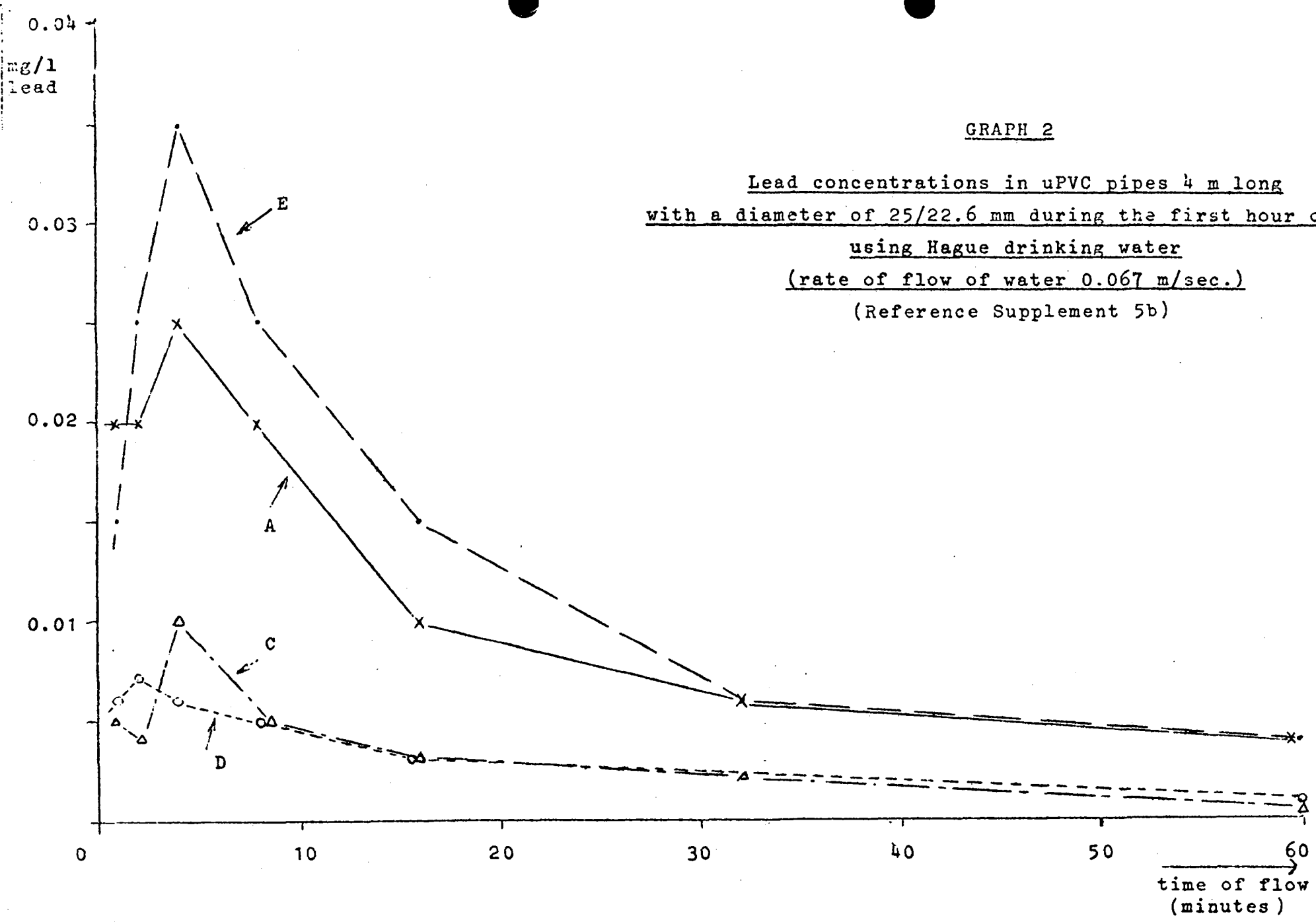


GRAPH I.

Lead concentrations in uPVC pipes 4 m long
with a diameter of 16/14 mm during the first hour of flow
using Hague drinking water
(rate of flow of water 0.067 m/sec.)
 (Reference Supplement 5a)

GRAPH 2

Lead concentrations in uPVC pipes 4 m long
with a diameter of 25/22.6 mm during the first hour of flow
using Hague drinking water
(rate of flow of water 0.067 m/sec.)
(Reference Supplement 5b)



Since stabilizers may be leached of uPVC at different rates depending on the nature of the stabilizer and the way of how the uPVC is processed, the test provides no indication of either the initial or the ultimate rates of leaching. The above mentioned test is based on the widely held belief that all the extractable lead stabilizers contain a lead rich larger at the surface of the pipe.

After having tested several extractants, a 0.5% nitric acid - 0.85% perchloric acid - was selected as extractant, because this extractant effectively leached lead compounds without effecting the uPVC material. From the investigations of Packham appeared that the time of agitation is less important than the number of extractions. The procedure proposed to include six extractions, each of 60 minutes.

The KIWA compared the testing procedures for lead leaching according to the I.S.O. method and the WRA. The "total" lead leaching according to the WRA method was compared with the "total" lead leaching according to the I.S.O. method and the lead concentrations during flow tests, using drinking water of the Hague (ref. 4). Table 4 gives the results. In so far the "total" lead leaching is concerned it was concluded that neither the WRA method nor the I.S.O. method correlate with the initial lead levels which appear after the first periods of standing directly after the installation of new uPVC pipe. As the lead concentrations are effected by the pH of the extractant and the lowest lead levels are to be expected at pH 7 - 8, the lead concentrations in the I.S.O. extracts (pH 4.6) are commonly higher in comparison with the lead levels after periods of standing using drinking water with a pH of about 7 - 8. It is to be expected in practice that the differences between the lead levels of the first and second extracts are in some way indicating the decrease in lead levels after successive periods of standing. Concerning the lead levels of the extracts, the I.S.O. method indeed simulates an "aggressive" type of drinking water.

As to the uPVC pipes which are included in the investigations of the KIWA (four different makes, three different diameters each) the "total" lead leaching calculated from the I.S.O. extracts (pre-flushing during 1 hour) amounted to 16 - 87% of that determined according to the WRA method using successive extractions for 1 x 1 hour and 3 x 1/2 hours. An almost similar comparison made by the WRA in four different makes of PVC pipe resulted in a recovery of 30 - 64%.

In order to determine the influence of the duration of the pre-flushing period on lead leaching according to the I.S.O. method (pre-washing during 1 - 6 hours) the integrated lead leaching during the first, the first 2, the first 4 and the first 8 hours of pre-washing with Hague drinking water has been determined for 8 different uPVC pipe of 4 different makes. The values are given in table 4 . It can be concluded that a considerable

quantity of lead has leached during the pre-flushing and that the effect is the greatest for pipes with the smallest diameter. The result of the test according to the I.S.O. is strongly effected by the period of pre-flushing.

Table 4 - Correlation between flow tests and extraction tests

1	2	3	4	5	6	7	8	9	10	11	12	13	14
		Lead leaching mg/100 cm ²						Lead concentration mg/l					
Manu- fac- turer	Dia- meter	WRA	ISO [#]	Hague water 10 x ext. 5 min. each	flow test Hague water		lead film deter- mined from bore tests	ISO		flow tests with Hague water			
					0-1 hour	0-24 hours		1st ext.	3rd ext.	max. du- ring flow 0-4 min.	after 16 min. of flow	after 24 hours flow and 48 hours standing	idem 5 min. flow and 72 hours standing
E	16/14	0.47	0.28	0.05	0.03	0.08	0.11	6.3	0.60	0.06	0.02	0.55	0.15
	25/22.6	0.41	0.30		0.04	0.18		4.2	0.53	0.04	0.02	0.32	0.23
C	16/14	0.25	0.20	0.05	0.02	0.14	0.14	4.9	0.45	0.03	0.01	1.00	0.32
	25/22.6	0.24	0.20		0.01	0.01		2.8	0.48	0.01	0.003	0.14	0.05
A	16/14	0.24	0.17	0.06	0.04	0.24	0.14	3.9	0.27	0.10	0.02	0.65	0.28
	25/22.6	0.20	0.11		0.03	0.04		1.0	0.43	0.03	0.01	0.41	0.33
D	16/14	0.14	0.02	0.02	0.01	0.02	0.16	0.13	0.16	0.03	0.009	1.05	0.85 ⁺
	25/22.6	0.09	0.03		0.01	0.03		0.16	0.17	0.007	0.003	0.16	0.36 ⁺

[#] 1 hour pre-washing

⁺ duplicate pipe after 5 min. flow and another 48 hours standing 0.06 mg/l

The WRA flushed samples of 25 mm bore uPVC pipe for periods up to eight hours, then they are extracted for six hours with 150 mg/l carbon dioxide solutions. The experiments were repeated by using acetic acid sodium acetate buffer and sodium bicarbonate solution as an extractant. Table 5 gives the lead concentrations of six hour extracts.

Table 5 The effect of flushing time on the extraction of lead from uPVC pipes

Flushing time (hours)	Mean lead content (mg/l) of 6-hour extract using		
	CO ₂	CH ₃ CO ₂ H/CH ₃ CO ₂ Na	NaHCO ₃
0	1.62	0.59	0.28
½	0.23	0.31	0.15
1	0.17	0.16	0.07
2	0.13	0.25	0.07
4	0.11	0.21	0.06
8	0.11	0.18	0.05
8 (static)	0.55	0.62	0.13

The results in table 5 show that the extraction levels decreased with increasing periods of flushing although the absolute levels of extraction differed according to the used extractant. In all cases the tendency of the results obtained after periods of flushing to level out for longer than one hour. Included in table 5 are the results of an experiment in which new pipe samples were filled with tapwater and allowed to stand for eight hours prior to extraction. The extraction levels in this experiment were three to four times greater than those which were obtained after flushing the pipes with tap water for the same period.

The WRA prefers no pre-flushing prior to the testing.

The KIWA prefers a short period of pre-flushing for example half an hour and an insertion into installation regulations for uPVC pipe of an obliged pre-flushing during the same period before the use.

7. Considerations

- 7.1 According to uPVC manufacturers the use of non-toxic stabilizers such as calcium and zinc compounds led to low output rates and short runs during the production. The produced pipe has inferior mechanical qualities. Toxic lead and tin containing stabilizers are used for the production of uPVC drinking water pipes. Lead containing stabilizers have almost exclusively been used in Europe up till now. Lead stabilized uPVC pipe cannot meet the NSF specifications in the U.S. and for this reason organo-tin stabilizers are exclusively used. Although many data are available on the lead leaching of lead stabilized uPVC pipe, this is not the case with organo-tin stabilized uPVC pipe. It is proposed that a similar survey for organo-tin stabilized uPVC pipe as is discussed in the discussion paper, should be realised by the NSF.
- 7.2 The work of KIWA and WRA has shown that the test procedures in lead leaching currently employed in the Netherlands and U.K. (as exemplified by the I.S.O. procedure) have provided a satisfactory measure of safety to drinking water in so far lead is concerned. While in some respects there is a scope for a future improvement of these procedures they can be recommended confidently for use at the present time as far as lead is concerned. When considering the leaching of toxic stabilizers from uPVC pipe in relation to the I.S.O. standard, it is essential that the physical properties of the pipe (e.g. impact strength, bursting strength) should be shown to conform to the standard as well as the results of extraction tests.

Future research at KIWA is directed to determine whether the behaviour of uPVC pipe manufactured in different parts of the world corresponds to that of pipe manufactured in the Netherlands and U.K. with respect to lead leaching. Other studies are being undertaken by the WRA to obtain more information on the long term migration of stabilizers from uPVC pipe.

In view of the available information the consequences of the use of toxic compounds for the manufacture of uPVC pipe to be used in developing countries should be taken into consideration.

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TECHNICAL INQUIRY REPORT

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TIR. No. 171.

THE DETERMINATION OF ACRYLAMIDE IN POLYELECTROLYTES

1. INTRODUCTION

Work in these laboratories has indicated serious discrepancies in the amounts of monomer extracted from acrylamide polymers and co-polymers by various extraction methods. The extraction procedure detailed in Sect. 2 of this report has been found to be satisfactory, giving identical results to analyses performed on aqueous solutions of polyelectrolytes. However, analysis of aqueous extracts by gas chromatography is normally only satisfactory if the polymer contains 0.5% acrylamide or more.

A gas chromatographic procedure for the determination of acrylamide was used in studying the efficiency of different methods of extraction and full details of this are given in Sect. 3 of this report. Although the recommended extraction procedure was designed to precede analysis by G.L.C., it may be used with slight modification with other types of analysis as mentioned in Sect. 2.2.

2. EXTRACTION OF ACRYLAMIDE FROM POLYELECTROLYTES

2.1. Procedure

Weigh out 1 g of polymer into a 1 oz McCartney bottle, add 10 ml (note 1) of a 20% water 80% methanol mixture (note 2) and screw down the cap firmly. Shake to disperse the polymer and transfer to a Microid flask shaker. Clamp horizontally, and shake vigorously for 24 hours (note 3). Allow the polymer to settle and take an aliquot for analysis (notes 4 and 5).

2.2. Notes

1. The polymer to solvent ratio is not critical, identical results were achieved using 2 g polymer to 10 ml solvent and 0.2 g polymer to 10 ml solvent. 1 g polymer to 10 ml solvent was the highest polymer to solvent ratio which gave a mobile slurry with all polymers tested.
2. Higher percentages of water in methanol give faster extraction of acrylamide but caused some polymers to gel. Lower percentages did not extract all the acrylamide. A 20% water 80% methanol mixture gave complete extraction of acrylamide, without causing any of the polymers tested to gel.
3. It is essential that no aggregation of the polymer particles is allowed to take place or poor extraction will result. The above vessel (McCartney bottle) and shaking methods were found applicable to all polymers tested. Some polymers were completely extracted in considerably less than 24 hours, but no polymer tested showed any increase in acrylamide recovery after this time.
4. Larger scale extractions will be necessary for some other types of acrylamide analysis. This is feasible provided that the above recommendations are adhered to, note 3 being particularly important.

5. Extracts deteriorated if stored on the bench for more than one or two days. Samples stored in a refrigerator, however, were still satisfactory after one week. Longer periods of storage were not tested.

3. THE ANALYSIS OF ACRYLAMIDE BY GAS CHROMATOGRAPHY

3.1. Instrument

Perkin-Elmer F11 equipped with flame ionisation detector, and glass columns. On-column injection was achieved by use of a 10 μ l Hamilton microsyringe (5 in. needle).

3.2. Column and conditions

Glass column 1 metre long by 3 mm internal diameter packed with 60-80 mesh, acid washed, dichlorodimethylsilane treated Chromosorb W, supporting 20% by weight of Carbowax 20M. The column is run at 170°C and 32 ml/min of N₂. Before use the column must be conditioned by running at 200°C (32 ml/min N₂) overnight.

3.3. Standard solutions

Solutions of acrylamide in a 20% water 80% methanol mixture made up at 0.01, 0.05, 0.2 and 2 mg/ml respectively.

3.4. Calibration of chromatograph

Inject 5 μ l of each of the above standards into the chromatograph (on-column injection) using amplifier attenuation settings to give peaks not greater in height than half scale. (On the above instruments 5 x 1, 20 x 1, 1 x 10² and 10 x 10² respectively). These injections correspond to 0.05, 0.25, 1.0 and 10.0 μ g acrylamide.

Estimate the areas of the peaks by multiplying the peak height by the peak width at half the peak height. The second parameter should be measured parallel to the sloping baseline constructed from the tail of the solvent peak, as shown in Fig. 1. This is important with the smallest amount of acrylamide injected.

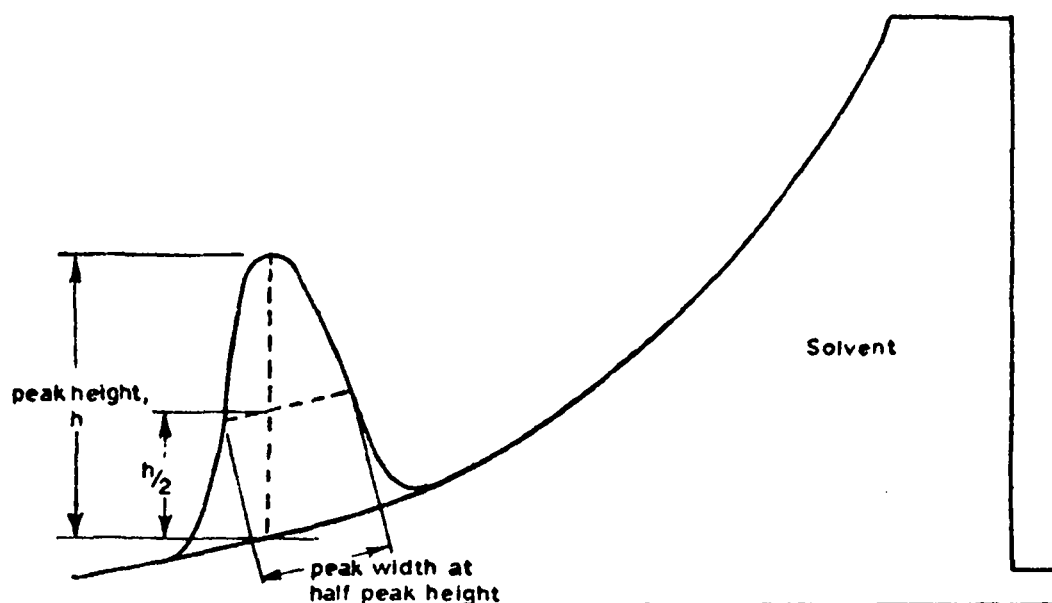


FIG. 1. ESTIMATION OF PEAK AREA

The relationship between amount of acrylamide injection (μg) and peak area (sq cm at an attenuation of 1) is non-linear on the above instrument, but an excellent straight line calibration can be achieved by the use of a log-log plot. This graph will cover monomer in polymer concentrations of 0.01 to 2% using 1 g polymer to 10 ml extracting solvent (20% water 80% methanol mixture).

3.5. Estimation of acrylamide in a sample extract

Inject 5 μ l of extract and estimate the area of the acrylamide peak using the above method. An attenuation setting should be chosen such that the peak height is less than half scale on the recorder. Read off the quantity of acrylamide present in the 5 μ l injection from the calibration graph. For a polymer to solvent ratio of 1 g to 10 ml the percentage of acrylamide in the polymer may be calculated as follows:

$$\% \text{ monomer} = 0.2X$$

where X = μ g of acrylamide in the injection.

3.6. Notes

1. On-column injection may not be necessary, but with the above instrument it gave the best peak shapes.
2. Other G.C. columns were tested:
 - 10% neopentylglycol succinate/AW DMCS Chromosorb W.
 - 10% Carbowax 20M/AW DMCS Chromosorb W.
 - 4% Carbowax 20M + 4% isophthalic acid/AW DMCS Chromosorb W.
 - 8% Carbowax 20M + 8% isophthalic acid/AW DMCS Chromosorb W.
 - 10% Versamid 900, /AW DMCS Chromosorb W.
 - 60-90 mesh Phasepak Q.

The recommended column gave the least solvent tailing and the best acrylamide peak shapes.

3. Other means of estimating peak areas were tried; only the recommended method gave a straight line calibration over the

the whole of the above range of acrylamide concentrations. Measurement of peak heights gave non-linear calibrations. Integration was not tried, but simple integration techniques would not be applicable to the lower quantities of acrylamide due to the sloping baseline created by the solvent tail.

4. Before injecting small quantities of acrylamide it was essential to check that the syringe did not contain residues of acrylamide from previous injections of larger quantities.
5. It was found that the calibration was stable for several days. However, it is recommended that it be checked every few injections.
6. In time the injection area of the column became fouled with non-volatile materials from extracts. This caused peak broadening and tailing. This could usually be cured by re-packing the first few inches of the column. If this was not successful a new column was prepared.
7. If solvents containing amounts of water greater than 20% were injected 'ghost' peaks could appear from previous injections. In these cases the solvent was repeatedly injected until the spurious peaks disappear.
8. Syringes were cleaned with water as well as the aqueous methanol to prevent their being jammed by deposits of polymer.
9. Standards deteriorated unless stored in the dark.