THE

ONTARIO WATER RESOURCES

COMMISSION

INVESTIGATIONS INTO THE CHARACTERISTICS, TREATMENT AND DISPOSAL OF INDUSTRIAL WASTES

at

UNIROYAL (1966) LIMITED, ELMIRA

1968

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REPORT ON INVESTIGATIONS INTO THE CHARACTERISTICS, TREATMENT AND DISPOSAL OF INDUSTRIAL WASTES

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by

Division of Industrial Wastes

ONTARIO WATER RESOURCES COMMISSION

SUMMARY

This report deals with the investigations of the Division of Industrial Wastes and the Divisions of Laboratories and Research into the sources, quantities, characteristics, treatment and disposal of wastes discharged from the Elmira plant of Uniroyal (1966) Limited and its effects on the Elmira Water Pollution Control Plant and Canagagigue Creek. The investigations cover a period from late 1966 to April, 1968.

Laboratory studies related to biological treatability and toxicity of the contaminated waste flow from this plant indicate that with up to 80% of the waste flow investigated, the wastes are readily treatable under laboratory conditions and non-toxic after treatment. Recommendations have been made with regard to raising the temperature of the wastes during the winter and improving the method of equalization within the lagoon system. It is hoped that these measures will bring conditions at the Elmira WPCP closer to those of the laboratory studies and achieve an increased degree of treatment efficiency together with reduced toxicity of the WPCP effluent.

A biological survey of the Grand River watershed in 1966 indicated that the Canagagigue Creek was almost devoid of aquatic biota downstream from Elmira to its confluence with the Grand River. This condition was found to originate just upstream from the Elmira WPCP outfall, which suggests the presence of sources of contamination other than the WPCP effluent. This report concludes that seepage from the waste equalization lagoon system at the Uniroyal plant and the 2,4-D waste pits are the most likely sources of this contamination and recommends that suitable control measures be taken by the Company.

In view of the complex nature of the wastes from this plant and the detrimental effects on the Elmira WPCP and Canagagigue Creek, this report recommends that other parameters for pollution control be used to

compliment the conventional BOD_5 and COD measurements. In addition to respiration rates, which are presently being done, analysis for total organic carbon should be implemented in the future in order to obtain additional knowledge about the efficiency of removal in the WPCP treatment processes.

INTRODUCTION

The Uniroyal (1966) Limited plant is located adjacent to Canagagigue Creek in the Town of Elmira. Canagagigue Creek has a long history of pollution related to the disposal of municipal and industrial wastes in Elmira. After a prolonged period of negotiations between the OWRC, municipal officials and the management of the then, Naugatuck Chemicals Division of the Dominion Rubber Company Limited, agreement was reached on the construction of a joint municipal and industrial waste treatment system. These facilities were completed in 1964. However, because of fibre problems from textile industries in Elmira and flooding of the plant grounds brought about by high water levels in the creek, it was not until the end of 1965 that wastes from the Uniroyal (1966) Limited plant were introduced into the joint treatment system. The complexity and toxicity of these chemical wastes could not have been fully realized in the original design of the facilities, since it is only recently that a moderately acceptable effluent is being produced and this only during the summer months and at the expense of occasional additions of raw sludge from the Waterloo Water Pollution Control Plant.

Furthermore, during the period 1963 to 1966, a number of local farmers have lost cattle from poisoning which has been attributed to the use of Canagagigue Creek for watering cattle. Recent biological survey data indicate the complete absence of all but a small number of the most

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pollution tolerant species of aquatic biota in the creek downstream from Elmira to its confluence with the Grand River and, significantly, the line of demarcation for this condition is the main cooling water discharge of the Uniroyal (1966) Limited plant upstream from the Elmira WPCP outfall.

It is, therefore, evident that this is one of the most persistent and outstanding pollution problems in Ontario. It is perhaps fortunate that downstream agricultural users of Canagagigue Creek have alternate sources of water and also that there is no significant urban development on the creek downstream from Elmira.

It is understandable, therefore, that this problem has been, and continues to be, studied in some depth by a number of Divisions of the OWRC and by the staff of Uniroyal (1966) Limited.

MANUFACTURING PROCESSES AND SOURCES OF WASTES

The Uniroyal (1966) Limited plant in Elmira is a diverse chemical manufacturing operation, producing a range of organic chemicals for the agricultural, rubber and plastics industries.

The following is a brief summary of the chemical reactions and manufacturing operations being carried out in the various processing buildings at the plant, including a brief description of the wastes produced.

Building No. 14 - Thiazole Building

Mercaptobenzothiazole (MBT) and derivative rubber chemicals are manufactured in this building. The MBT base material is produced by reacting aniline and carbon disulphide in an autoclave. The sodium salt is then produced by the addition of caustic soda. The excess alkali is discharged as the causticizer decant prior to the addition of sulphuric acid to precipitate the MBT sodium salt. This precipitate slurry is then transferred to Building No. 36 to be filtered, washed, dried and packaged or returned to Building No. 14 for further processing.

The MBT sodium salt may be reacted with zinc sulphate to produce MBT zinc salt (trade name OXAF), oxidized with sodium nitrite and sulphuric acid to produce benzothiazyl disulphide (trade name MBTS) or reacted with cyclohexamine to produce N-cyclohexyl-2 benzothiazole-sulphenamide (trade name DELAC-S).

In addition, two derivatives of dimethyl dithiocarbamate (methyl ADAM), produced in Building No. 15, may occasionally be produced. The methyl ADAM may be reacted with sodium nitrite and sulphuric acid to produce a thiuram disulphide (trade name TUEX) or reacted with sodium cyanide to produce a thiuram monosulphide (trade name MONEX).

The waste effluents from the manufacture of the MBT derivatives are usually precipitate washings which contain sodium salts, such as sulphates, sulphides, nitrates and nitrites.

Excess reagents and sodium sulphate or sodium thiocyanate are present in the wastewaters from the preparation of the ADAM derivatives.

Building No. 15

Two different types of compounds are manufactured in this building, the ADAM based rubber chemicals previously mentioned and chlorinated phenol herbicides.

2,4,-Dichlorophenol, manufactured in Building No. 25, is reacted with an alcohol to give a 2,4-D ester. The acid and ester derivatives of 2,4,5,-Trichlorophenol are prepared in a similar manner. All of these compounds are sold as herbicide materials in a variety of formulations.

The wastewaters from these operations consist of filtrate washings from the acid production and separator underflow. These wastewaters

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contain the soluble components from the reactions, usually phenolics and acids and alkalis.

Dimethylamine and carbon disulphide are reacted to produce dimethyl dithiocarbamate (methyl ADAM) in the ADAM side of Building No. 15. The methyl ADAM is usually produced as the sodium salt and consequently the wastewaters are largely associated with the causticizing and subsequent acidification common to this procedure. Ethyl and butyl ADAM are produced in the same way as the methyl ADAM except that ethyl and butyl amines replace dimethylamine.

Dithiocarbamate zinc salts may be prepared from all of these ADAM base compounds by reacting with zinc sulphate to give METHAZATE from methyl ADAM, ETHAZATE from ethyl ADAM and BUTAZATE from butyl ADAM. The wastewaters from these reactions usually contain sodium sulphate and traces of zinc sulphate. In a similar manner, ethyl ADAM may be reacted with sodium selenite to give ethyl SELEZATE.

Addition compounds of methyl and ethyl ADAM (TUEX and ethyl TUEX) may also be produced, as in Building No. 14, by reacting with sodium nitrite and sulphuric acid. Wastewaters containing sodium sulphates and nitrates are discharged from these processes.

Building No. 25

Phenol derivatives are manufactured in this building. Dichlorophenol is produced by direct chlorination of phenol. Rubber chemicals, based on alkyl derivatives of phenol, are prepared by reacting a phenol with the required hydrocarbon in the presence of a catalyst. Thus, nonene is reacted with p-cresol to produce the alkylated derivative ESSU. This may be reacted with paraformaldehyde to produce a bimolecular addition, compound NAUGAWHITE. The nonene alkyl derivative of phenol (UMNO) is

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reacted with phosphorus trichloride to produce an alkylated aryl phosphate POLYGARD. These alkylated phenol products are recovered from the reaction mixtures by vacuum and steam distillation. The residual organics are burnt and by-product hydrochloric acid from the manufacture of POLYGARD is converted into commercial muriatic acid. A caustic fume scrubber on the dichlorophenol process is the major contaminated waste and this is retained in a sump and surface oil skimmed off prior to disposal. Other wastewaters consist of cooling and general wash waters.

Building No. 33

Various grades of polyester resins (VIBRINS) are manufactured in this building. The reactions involved are essentially the condensation of a glycol with maleic or phthalic anhydride followed by modification of the product with styrene in the presence of a catalyst. Water liberated in the reaction is discharged to the atmosphere as vapour. The main wastewaters consist of reactor and condenser cooling waters, reactor washings and other floor and equipment washings.

Building No. 28

A number of aromatic amine antioxidant rubber chemicals are manufactured in this building. These fall into three general categories, depending upon the type of compound reacted with the aromatic amine; namely, aliphatic carbonyl compounds, aliphatic hydrocarbons or phenols.

Diphenylamine is reacted with acetone in the presence of an iodide catalyst to yield a condensation product BLE. Aniline is reacted with butyraldehyde to produce a condensation product BEUTENE. Wastewaters from these reactions are largely cooling water and wash water, containing traces of reactants and catalysts.

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Diphenylamine is reacted with nonene or di-isobutylene to yield the aromatic amine hydrocarbon derivatives POLYLITE and OCTAMINE, respectively. Wastewaters from these reactions consist of cooling waters and wash waters containing traces of reactants and aluminum hydroxide from the aluminum chloride catalyst.

Aniline is reacted with hydroquinone or beta-naphthol in the presence of a catalyst to produce the phenol derivatives JZF (or ERER) and PBNA respectively. The products from these reactions are recovered by distillation and the wastewaters consist mainly of cooling and wash waters.

Building No. 36

Products manufactured in Building No. 14 are filtered and dried in this building. The wastewaters from these operations are mainly filtrate, containing mother liquor and washings, and general wash water.

Building No. 37

This building is used exclusively for the manufacture of aromatic diamine antioxidant rubber chemicals - FLEXZONES.

Diphenylamine is reacted with sodium nitrite and sulphuric acid to produce the corresponding diazonium salt. This is converted to the sodium salt by addition of alkali and then catalytically reduced with hydrogen to the corresponding phenylene diamine intermediate UBOB. The UBOB intermediate may then be reacted with one of three aliphatic ketones to produce the required FLEXZONE product.

Wastewaters from this building consist of cooling waters, equipment and floor washings and periodic discharges of wash waters from a recovery still used to recover solvent used in the preparation of the UBOB intermediate.

The total number of products manufactured at this plant exceeds two hundred. However, it is evident from the foregoing that these may be broken down under a small number of general headings which broadly classify the products by their chemical structure. Table I indicates these general headings and the equivalent brand names of the main products manufactured.

TABLE I

Type	Brand Name
Chlorinated phenols and phenol esters	2,4,-D Acid
	2,4,-D MBE
	2,4,-D IOE
	2,4,5,-T Acid
	2,4,5,-T MBE
	2,4,5,-T IOE
Alkylated phenols	Polygard
	ESSO
	UMNO
	Naugawhite
Aromatic amines	UBOB
	Flexzone 3C, 5L, 6H and 7L
	Flexamine Crude
	Aminox - BLE
	JZF - ERER
	Beutene
	Octamine
	Polylite
	PBNA
Aromatic thiazoles	MBT
	MBTS
	DELAC - S
	OXAF
Aliphatic dithiocarbamates	Methyl ADAM
	Ethyl ADAM
	Butyl ADAM
	Methazate
	Ethazate
	Butazate
	Ethyl selezate

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Type	Brand Name
Aliphatic thiuram sulphides	Monex Tuex Ethyl Tuex
Polyesters	Vibrins

In almost all cases, the manufacturing operations are carried out in batch reactors and the product obtained by distillation or crystallization from an acid media. Consequently, the contaminated wastes usually consist of still residues, product and equipment washings, recrystallization mother liquors or filtrate washings.

Cooling waters are almost completely segregated from the contaminated waste flow and approximately 1,000,000 gpd are discharged directly to Canagagigue Creek.

Residual tars from reactors or stills are disposed on land or are burnt in a process waste burner.

Other liquid wastes include boiler blowdown and sanitary sewage. Boiler blowdown is discharged to the creek and sanitary sewage is discharged to municipal sanitary sewers.

Process water, about three quarters of the cooling water and domestic water are obtained from the Elmira P.U.C. and this is augmented by cooling and boiler feed water obtained from Canagagigue Creek.

Table II indicates the sources and volumes of the major contaminated waste flows from this plant.

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Table II

Sources and Volumes of

Contaminated Wastewaters

Source		Average Waste Flow Igpd
Bldg. 14 (Thiazoles)	- Causticizer Decant	1,300
Bldg. 15 (A.D.A.M. side	- Press filtrate	800
- Thiocarbamates	- Press washings	9,200
and Thiurams)	- Scrubber	15,000
Bldg. 15 (2,4,-D side - Chlorinated phenol esters)	- Acid wastewater	17,500
Bldg. 25 (Chlorinated and alkylated phenols)	- Sump wastewater	12,000
Bldg. 28 (Aromatic amines)	- Sump wastewater	6,000
Bldg. 33 (Polyester resins)	- Sump wastewater	26,000
Bldg. 36 (Thiazoles)	- Sump wastewater	19,000
Bldg. 37 (Aromatic amines)	- Sump wastewater	20,000
Bldg. 19 (Pilot plant)	- Sump wastewater	40,000 (estimated)
Sanitary sewage		7,000
	TOTAL	173,800

These waste flows are approximate average figures and tend to vary with the nature and the production of the particular compounds in each building. In addition, there is an undetermined volume of general wash water discharged daily. The total contaminated waste flow from the plant to the Elmira sewage treatment plant may vary between 140,000 gpd and 260,000 gpd.

WASTE DISPOSAL

The diagram on page 12 indicates the general plant layout, the sewer system and the pretreatment works. Pretreatment of the contaminated waste flow is a condition of the original agreement between the OWRC, the Town of Elmira and the Dominion Rubber Company Limited setting up the joint treatment system. These facilities include an equalization lagoon system, a 177,000 gallon circular mixing and equalization tank and neutralization equipment. The lagoon system has been considerably enlarged since the original agreement was instituted and now has a total capacity of about 3 million gallons. The lagoon system is designed to balance out daily fluctuations in waste strength and volume and also serves as a primary sedimentation and oil removal facility. However, certain waste flows, in particular the effluent from the Building No. 8 wastewater sump, may be discharged directly to the pretreatment facilities at times when the low temperature of the lagoon effluent becomes critical to the biological processes at the sewage treatment plant.

There are two main collection points within the plant for the contaminated wastewaters. The waste sump at Building No. 8 receives wastewaters from Buildings No. 19, 25, 33 and 37; the general waste sump adjacent to Building No. 16 receives wastes from Buildings No. 14, 15 and 36. Wastewater from Building No. 28 and the 2,4,-D wastes from Building

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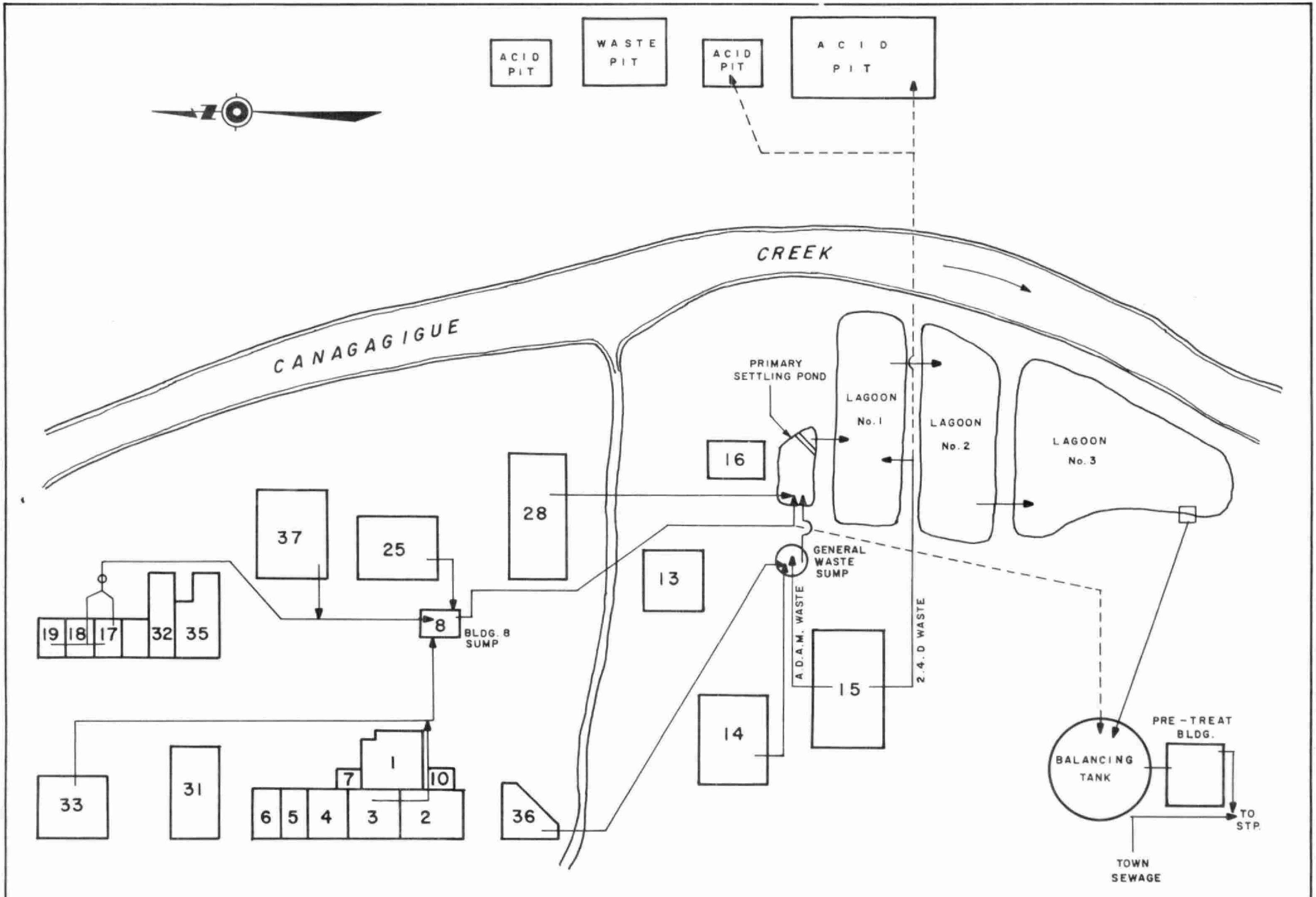

UNIROYAL (1966) LIMITED – ELMIRA – WASTE DISPOSAL SYSTEM

NOT TO SCALE
DWG No: 67-IR-98

No. 15 are discharged directly to the lagoon system. Wastes containing cyanides, from the manufacture of MONEX in Building No. 14, are retained in a holding pond before being slowly discharged to Lagoon #1.

DETAILS OF SURVEY

Personnel Participating

OWRC

Mr. R. A. Abbott, Division of Industrial Wastes
Mrs. Y. Lambert, Biology Branch, Division of Laboratories
Mr. J. Smart, Division of Research

Uniroyal (1966) Limited

Mr. R. E. Mills, Plant Chemist

Personnel Interviewed

Mr. A. Gorman - Plant Manager
Mr. R. E. Mills - Plant Chemist

General Operating Data

Number of Employees: 270

Operating Schedule: 24 hours per day
5 - 7 days per week

Water Consumption:	Process	180,000 gpd
	Cooling and Boiler Feed	1,100,000 gpd
	Sanitary	7,000 gpd
Sources:	P.U.C.	1,007,000 gpd
	Canagagigue Creek	280,000 gpd

Sampling and Analysis

Data collected for this survey were obtained over a period of several months during 1966, 1967 and 1968. Waste samples for bio-assay analysis were collected during September and November, 1966, during

January, February and March of 1967 and during February and March, 1968.

Industrial waste samples for chemical analysis were obtained on June 28, 29 and 30, 1967. All samples, with the exception of the cooling water samples, were composites obtained from automatic samplers or obtained by combining equal aliquots of the particular waste flow, taken at regular intervals. All samples for chemical analysis were submitted to the OWRC laboratory for analysis for BOD, solids, pH, COD, phenols, total nitrogen, sulphide and sulphate in accordance with the procedures described in "Standard Methods for the Examination of Water and Wastewater", 12th edition, published by the U. S. Public Health Association.

In a number of instances, duplicate waste samples were submitted to the OWRC, Division of Research for biological treatability and subsequent bio-assay analysis by the Biology Branch of the Division of Laboratories. The purpose of the treatability and bio-assay studies was to establish the most toxic and non-treatable waste flows in the plant, so that these could be isolated from the main discharge for alternative treatment or disposal and thus improve the treatment efficiency of the Water Pollution Control Plant and reduce the toxicity of the effluent.

These studies are being continued. The results to date are discussed in the section which follows.

Chemical characterization of the contaminated waste flow is being carried out by the Industrial Waste Section of the Chemical Laboratory in an attempt to identify the predominant components or groups of components present in the wastes before and after treatment. It is hoped that these data can then be related to the toxicity and treatability studies previously mentioned.

ANALYTICAL RESULTS

See following pages.

UNIROYAL (1966) LIMITED - ELMIRA

Date Sampled: June 28, 1967

All analyses except pH reported
in ppm unless otherwise indicated

Lab. No.	5-Day BOD	Solids			COD	pH at Lab.	Total Kjeldahl as N	Nitrite as N	Free Ammonia as N	Sulphates as SO_4	Sulphide as H_2S	Phenols in ppb
		Total	Susp.	Diss.								
T-1964	1.70	3,526	161	3,365	3,090	4.0	28.0	0.00	0.79	-	-	3,000
T-1965	835.	116,088	98	115,990	1,990	1.8	-	-	-	-	-	5,000
T-1966	315.	27,756	95	27,661	21,600	9.3	280.	0.02	Interference	6,687	2.0	-
T-1967	115.	1,200	134	1,066	5,730	7.4	120.	0.36	"	362	250.	-
T-1968	950.	2,164	340	1,824	3,500	8.5	23.5	0.08	"	597	0.3	-
T-1969	139.	199,272	416	198,856	30,000	10.2	536.	0.01	"	14,036	0.1	-
T-1970	500.	3,118	187	2,931	4,720	7.7	31.	0.08	"	724	0.0	1,500
T-1971	66,000	22,484	505	21,979	85,000	10.5	6.60	-	-	-	-	-
T-1972	360.	1,496	111	1,385	9,500	6.5	-	-	-	-	340.	-

T-1964	1	Building No. 28 Wastes	Composite 10:30 to 2:30
T-1965	2	Building No. 15 2,4,-D Wastes	Grab 11:00 a.m.
T-1966	3	General Waste Sump Discharge at Bldg. 16	Composite 10:30 to 3:00
T-1967	4	Building No. 14 Wastes	Composite 10:30 to 3:00
T-1968	5	Building No. 15 (clean-up)	Composite 10:30 to 3:00p.m.
T-1969	6	Building No. 36 Wastes	Composite 10:30 to 3:00
T-1970	7	Building No. 8 Sump Discharge	Composite 10:30 to 3:00
T-1971	8	Building No. 15 (clean-up)	Grab 11:30 a.m.
T-1972	9	Building No. 14 (Causticiser Decant)	Grab 11:30 a.m.

UNIROYAL (1966) LIMITED - ELMIRA

Date Sampled: June 29, 1967

All analyses except pH reported
in ppm unless otherwise indicated

Lab. No.	5-Day BOD	Solids			pH at Lab.	COD	Phenols in ppb	Total Kjeldahl as N	Sulphide as H_2S	Sulphate as SO_4
		Total	Susp.	Diss.						
T-2001	135	2,048	302	1,746	9.4	7,800	2,000	150.	0.0	5,024
T-2002	122	19,364	182	19,182	9.1	6,370	4,000	250.	0.75	4,806
T-2003	280	26,274	39	26,235	9.4	13,700	12,000	410.	5.0	6,617
T-2004	265	26,260	44	26,216	9.2	11,200	12,000	395.	2.0	6,049
T-2005	278	7,880	55	7,825	8.5	4,260	3,200	130.	0.0	1,951
T-2006	360	18,660	58	18,602	9.2	7,900	3,000	250.	0.1	4,448
Avg.	240	16,748	113	16,635		8,540	6,030	264	1.31	4,816
T-2007	1,200	1,858	69	1,789	6.6	9,100	3,200	8.30	0.1	4,848

T-2001	1	General waste sump - composite 1500 hrs. - 2100 hrs. - June 28
T-2002	2	" " 2100 hrs. - 2400 hrs. - June 28
T-2003	3	" " 2400 hrs. - 0300 hrs. - June 29
T-2004	4	" " 0300 hrs. - 0600 hrs. - June 29
T-2005	5	" " 0600 hrs. - 1000 hrs. - June 29
T-2006	6	" " 1500 hrs. June 28 - 1000 hrs. June 29
T-2007	7	Building #8 waste sump - composite - 1100 hrs. - 1400 hrs.

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Date Sampled: June 30, 1967

All analyses except pH reported
in ppm unless otherwise indicated

Lab. No.	5-Day BOD	Solids			COD	Phenols in ppb	Total Kjeldahl as N	Free Ammonia as N	Sulphide as H_2S	Sulphate as SO_4
		Total	Susp.	Diss.						
T-2041	560.	9,598	25	9,573	1,210	16,000	35.0	9.84	0.0	3,827
T-2042	1.5	656	8	648	18	10	-	-	-	-
T-2043	0.8	720	8	712	4	20	-	-	-	-
T-2044	0.5	648	1	647	15	0	-	-	-	-
T-2045	0.9	708	5	703	4	8	-	-	-	-
T-2046	0.5	710	1	709	7	8	-	-	-	-

T-2041	1	Total plant effluent after neutralization.
T-2042	2	Cooling discharge to creek at powerhouse.
T-2043	3	Cooling discharge to creek #1 at Building 25.
T-2044	4	Cooling discharge to creek #2 at Building 25.
T-2045	5	Cooling discharge to creek #3 at Building 25.
T-2046	6	Cooling discharge to creek at Building 37.

UNIROYAL (1966) LIMITED - ELMIRA

Date Sampled: August 3, 1967

All analyses except pH reported
in ppm unless otherwise indicated

Lab. No.	5-Day BOD	Solids			pH at Lab.	COD	Nitrogen Kjeldahl as N	Sulphide as H_2S	Free Ammonia as N
		Total	Susp.	Diss.					
T-2555	30.	2,298	23	2,275	7.9	182	31.0	0.0	26.4
T-2555	1	Sewage treatment plant effluent.							

DISCUSSION OF FINDINGS

In this section the general waste characteristics, waste loadings, the Elmira WPCP and the biological treatability and toxicity studies will be discussed separately.

General Waste Characteristics

At the outset, it must be appreciated that the conventional parameters of pollution, BOD, COD and suspended solids, are questionable tools in assessing the characteristics of wastes from this plant. Both the BOD and COD tests are subject to interference and misinterpretation. Biochemical oxygen demand (BOD_5) is a measure of the oxygen depletion effect a waste may exert on a receiving stream and indicates the oxygen requirement of the waste for biological treatment. The standard test is usually carried out at 20°C for an incubation period of five days. This pre-supposes that the waste in question undergoes, almost complete degredation under the conditions of the test. Also, the use of a bacterial seed culture which is acclimatized to the waste in question is essential to obtain meaningful results. None of these conditions have been satisfied in the BOD analysis of many of the samples taken during this survey. Many of the wastes contain complex mixtures of organic chemicals which may not degrade biochemically within five days. In addition, the BOD analyses carried out at the OWRC laboratory have been conducted with municipal sewage as a seed culture. Consequently, part of the five-day incubation period has most likely been utilized in developing a culture from the domestic sewage seed which is effective in assimilating the complex organics present in the waste.

The chemical oxygen demand (COD) test involves digestion of the sample in the presence of a strong oxidizing agent and the oxidizing agent consumed is expressed as molecular oxygen. The test may be interpreted as the total or ultimate oxygen demand. However, certain organic chemicals, particularly benzene and its derivatives and certain cyclic nitrogen hydrocarbons, are resistant to attack by strong chemical oxidizing agents. Some of these compounds are degradable biochemically and would therefore exert an oxygen demand on the receiving stream or treatment works, which is not indicated by the COD test. Many of the raw materials and products likely to be present in the wastes from this plant fall into this category.

It is, therefore, evident that the interpretation of the BOD and COD analyses and their relationship to the toxicity of the wastes are limited. It is conceivable that wastes with low COD or BOD analyses may contain significant amounts of organic chemicals which are toxic to aquatic life and inhibit the biological processes in the sewage treatment plant.

With these considerations in mind, the following observations regarding the characteristics of the wastes discharged from this plant are presented.

The variability of the waste discharge from the general waste sump at Building No. 16, containing wastes from Buildings No. 14, 15 and 36, is clearly reflected in the analytical results of samples T-2001 to T-2006. COD analyses range from 6,370 ppm to 13,700 ppm, while BOD values vary from 122 ppm to 360 ppm. A concentrated discharge of phenolic wastes between midnight on June 28 and 6 a.m. on June 29 is evidenced by the high phenols analysis of the wastes during this period. The concentrations of sulphides, sulphates and total nitrogen and the COD of the waste also vary accordingly.

However, in comparing the results of samples T-1966 and T-2006, it becomes evident that with the exception of the COD analysis, the waste-waters from the general waste sump did not vary greatly over the two-day

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sampling period. Thus, it appears that, although fluctuations in waste strength occur within a 24 hour operating period, the average waste strength does not vary markedly from day to day.

The presence of high concentrations of phenolics in this waste stream is difficult to explain on the basis of the reported operations being carried out in the buildings contributing to the waste flow. Phenolics are associated with operations in Buildings No. 25, 28 and the 2,4,-D side of Building No. 15, all of which do not normally discharge wastes to this sump. However, carryover of phenolic bearing wastes from the 2,4,-D side of Building No. 15 or interference in the phenol determinations by amino compounds present in the wastes from Buildings No. 14, 36 and the A.D.A.M. side of Building No. 15 may both be contributing factors in the high phenols result of the samples from this waste sump. It was subsequently reported by the Company that the waste being discharged from Building No. 15 to this sump consisted mainly of condenser cooling water from the 2,4,-D side.

A further variable factor is the quality and quantity of clean-up washings present in the waste discharges from all of the processing buildings. This may be illustrated by the analytical results of samples T-1968 and T-1971 for June 28. It is clear from these results that a very strong waste was discharged from Building No. 15 at about 11:30 a.m. This was subsequently attributed by Company personnel to a clean-up operation following the production of a special chemical. This cannot, therefore, be regarded as a typical clean-up operation. Company officials nevertheless admit that clean-up wastes are a significant, but undetermined, source of contaminants.

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In examining the wastewaters being discharged to the general waste sump, wastes from Building No. 14 and 36 are of most significance, since production was being carried out in these buildings during this survey. The continuous waste discharge from Building No. 14 (Sample T-1967), is a small volume of cooling and wash waters, with an infrequent batch discharge of causticizer decant (see process description). The causticizer decant (Sample T-1972) is the most contaminated waste from this source and largely accounts for the high sulphide content and consequent high COD of the total waste flow from this building.

Building No. 36 contributes a substantial waste flow to the general waste sump from the purification and filtration of the products from Building No. 14. The high dissolved solids, COD, nitrate and sulphate content of this waste (see analytical results of Sample T-1969) reflects the presence of mother liquor and washings from the filtration of the crystalline products.

The analytical results of the sample of the wastes being discharged from Building No. 28 (Sample T-1964) illustrates the difficulties in interpreting BOD and COD analyses discussed at the beginning of this section. The BOD analysis of this sample is obviously subject to interference, possibly by the low pH, since the high COD suggests that the BOD should be much higher than the indicated 1.7 ppm. COD, nitrogen and phenols analyses for this sample are compatible with the nature of the operations being carried out in this building.

Low pH does not appear to be an interfering factor in the BOD analysis of the 2,4,-D waste sample from Building No. 15 (Sample T-1965). It may be that the BOD analysis of this sample is subject to interference and the actual BOD is higher than the indicated 835 ppm. This is impossible to verify. The COD analysis suggests that this BOD figure is

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reasonable, but the high dissolved solids content could be interpreted as soluble organic material and therefore capable of exerting a substantial oxygen demand.

During this survey, wastes discharged from the Building No. 8 sump were contributed by Buildings No. 25, 33 and 19. Building No. 37, which also contributes to this waste flow, was not operating and, therefore, wastes from the manufacture of rubber chemicals (Flexzones) were not present in the discharge from Building No. 8 sump.

Wastes discharged from Building No. 19 are difficult to identify, since operations in the building involve research and pilot plant development of new products.

The main identifiable waste flows contributing to the Building No. 8 sump discharge arise from the manufacture of polyester resins (in Building No. 33) and phenol and amine derivatives (in Building No. 25). The presence of wastes from these sources is confirmed by the COD and phenols content of the Building No. 8 sump discharge (Sample T-1970 and T-2007).

The variation in the strength of the samples of the waste discharge from Building No. 8 sump taken on June 28 and 29 is difficult to explain, except on the basis of an unidentified high strength discharge from Building No. 19. The analyses for BOD, COD and suspended solids for the June 29 sample (T-2007) are approximately double those for the June 28 sample (T-1970). The pH and sulphate content of the June 29 sample suggest that a strong acid waste was discharged to the Building No. 8 sump during this sampling period, although this is not compatible with the corresponding dissolved solids analysis.

There is little direct relationship between the analytical results of the total plant effluent sample (T-2041) and the component

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waste streams represented by the analytical results of the in-plant samples taken during this survey. Due to the retention period in the waste lagoons, the total plant effluent represents component waste streams discharged several days before this survey was undertaken. Nevertheless, certain general conclusions can be made since company personnel report that the general characteristics of the total plant effluent have remained relatively constant for longer periods since the lagoons were put into operation.

It is notable that there is a complete absence of sulphide in the total plant effluent (Sample T-2041). This may be the result of aerobic oxidation to sulphate in the lagoons or the loss of H_2S to the atmosphere from the decomposition of sulphides by low pH conditions in the lagoons. The free ammonia content of this sample is difficult to explain on the basis of the concentrations found in the in-plant waste samples. Bearing in mind the discrepancies likely to be found between the in-plant samples and the total plant effluent analyses, it is possible that amino or nitrite compounds present in the wastes may be reduced to ammonia in the lagoons, or that amino compounds, after retention in the lagoons, are being determined as free ammonia.

The cooling water discharges from this plant, as indicated by the analytical results for Samples T-2042 to T-2046, appear to be compatible with OWRC objectives, although the trace levels of phenols and COD in certain of these samples suggest that contaminants have not been completely eliminated from the cooling water system.

As has been previously mentioned, boiler blowdown is periodically discharged to the creek. This waste is known to be high in suspended solids, phosphates and alkalinity and should therefore be discharged with the

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other contaminated wastes from this plant.

Waste Loadings

It is evident from the table on waste loadings, Table III, that there is no correlation between the waste loadings of the total plant effluent from the equalization lagoons and the sum of the in-plant waste flows sampled during this survey. This is understandable in view of the fact that the residence time in the lagoons is up to ten days and, therefore, the effluent is only representative of in-plant conditions as much as ten days prior to sampling.

In addition, it is reasonable to expect reductions in suspended solids, COD and BOD to occur in the lagoons as a result of settling and biochemical and/or chemical oxidation respectively, or the loss of volatile organics to the atmosphere resulting in reductions in COD.

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TABLE III

Summary of Waste Loadings

Waste	Flow gpd	BOD lbs/day	COD lbs/day	Susp. Solids lbs/day	Phenols lbs/day	Nitrogen lbs/day
Building 14	2,000	2	115	3	-	2
Building 36	15,000	21	4,500	62	-	80
Building 15 (A.D.A.M.)	25,000*	-	90*	10*	-	-
Sub Total	42,000	23	4,705	75	-	82
General Waste Sump	33,000	80	2,850	37	0.2	88
Building 15 (2,4,-D)	20,000	167	398	20	0.1	-
Building 8 Sump	80,000	400	3,770	56	0.1	24
Building 28	7,500	<0.1**	230	12	0.2	2
Total	140,500	647	11,953	125	0.6	196
Total Plant Effluent	180,000	1,008	2,578	45	29	63

* Estimates from Company data. This process was not in operation during this survey.

** This figure is believed to be low due to interference in the BOD analysis.

N.B. Flow measured and/or estimated on days of survey and do not agree necessarily with average figures in Table II.

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Analytical data for the Uniroyal waste flow to the sewage treatment plant for the period January to April, 1967 are summarized in Table IV. It is evident from this table, that in spite of the equalization provided by the lagoon system, the BOD and suspended solids content of the wastes varied significantly from week to week during the period covered. However, the effect of the lagoon system in terms of equalization of waste strength is best illustrated by the graph on page 29. The lagoon system was put into operation in September, 1966 and it can be seen from the graph that the waste strength in terms of dissolved solids fluctuated widely from day to day and from week to week, prior to this. It is, nevertheless, evident that in spite of the improved equalization provided by the lagoon system, fluctuations in the strength of the lagoon effluent still occur, which probably reflect much larger changes in the strength of the raw wastes from the Uniroyal plant. This may be a factor in the continuing difficulties encountered at the Water Pollution Control Plant in treating this waste flow.

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TABLE IV

Uniroyal Waste Data*   January to April, 1967

Week Ending		Average Flow mgd	Average BOD ppm	Average BOD lbs/day	Average Susp. Solids ppm	Average Susp. Solids lbs/day
January	7	0.122	635	770	108	132
	14	0.147	1,150	1,690	111	163
	21	0.153	618	950	146	222
	28	0.153	800	1,220	134	202
Average		0.144	801	1,157	125	180
February	4	0.164	575	940	55	90
	11	0.177	888	1,570	140	250
	18	0.177	980	1,730	142	252
	25	0.164	673	1,110	206	338
Average		0.171	779	1,337	136	232
March	4	0.186	515	960	206	384
	11	0.181	631	1,140	138	250
	18	0.190	540	1,050	82	156
	25	0.188	720	1,360	144	271
Average		0.186	601	1,127	142	265
April	1	0.166	755	1,250	183	304
	8	0.194	425	825	95	184
	15	0.212	616	1,301	43	91
	22	0.192	645	1,240	84	161
	29	0.187	725	1,360	92	172
Average		0.190	633	1,195	99	182

* Project Status Report
OWRC Division of Plant Operations
June, 1967

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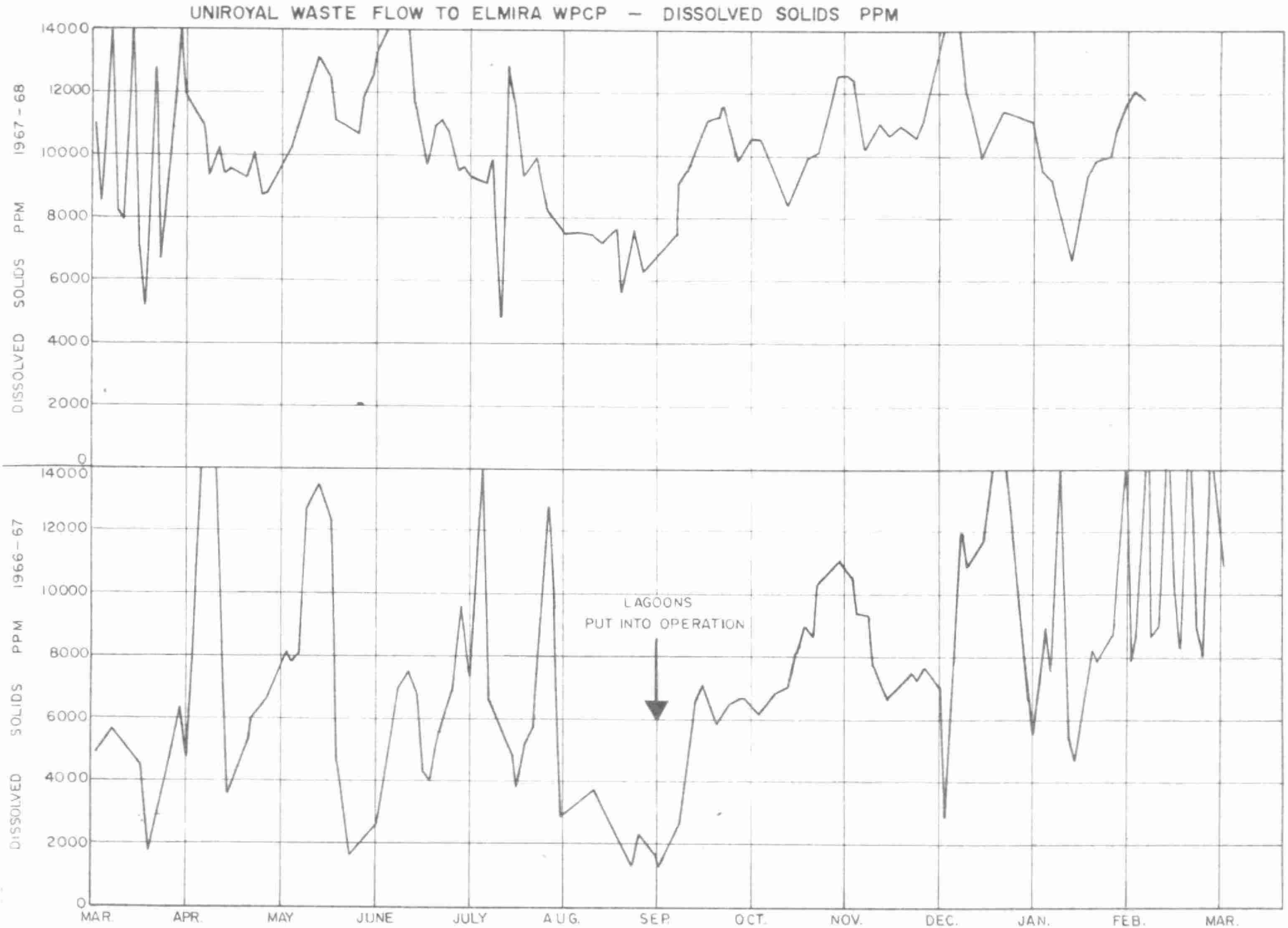

UNIROYAL WASTE FLOW TO ELMIRA WPCP — DISSOLVED SOLIDS PPM
1967 - 68
DISSOLVED SOLIDS PPM
14000
12000
10000
8000
6000
4000
2000
0
1966 - 67
DISSOLVED SOLIDS PPM
14000
12000
10000
8000
6000
4000
2000
0
LAGOONS
PUT INTO OPERATION
MAR.
APR.
MAY
JUNE
JULY
AUG.
SEP.
OCT.
NOV.
DEC.
JAN.
FEB.
MAR.

Sewage Treatment

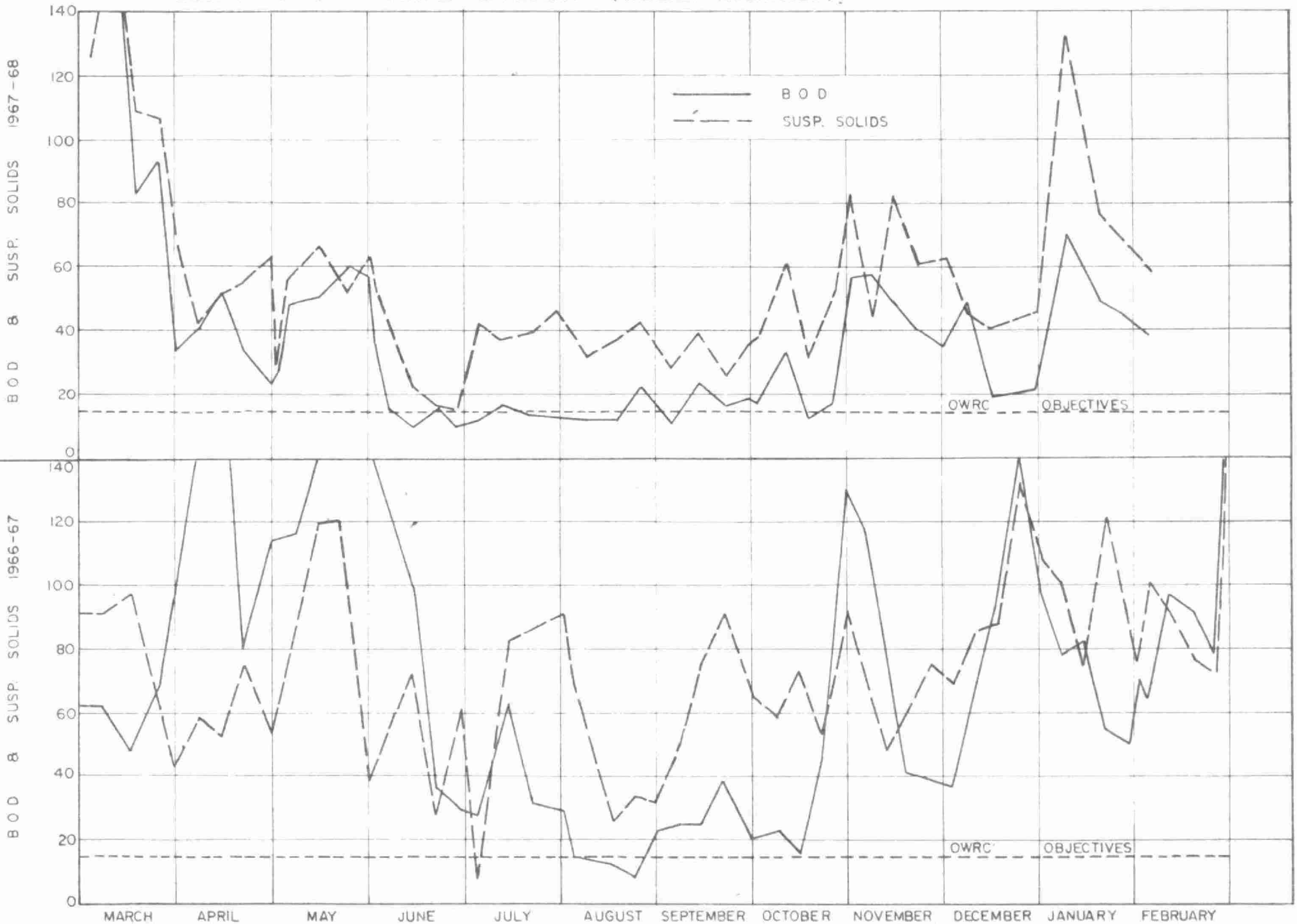
A detailed investigation of the operations and treatment efficiency of the Elmira Water Pollution Control Plant is being conducted by the Technical Advisory Services Branch of the Division of Research. Recommendations were made in 1966 regarding changes in operating procedures and minor modifications to the plant which would enable it to be operated almost as a completely mixed, high solids, activated sludge system. Initially, these changes resulted in improved effluent quality during the period December 1, 1967, to February, 1968, over previous years. However, conditions again deteriorated in mid-February and this was subsequently attributed to a shock loading of toxic waste, possibly from MONEX production (see Appendix VII).

It is interesting to note that the use of a completely mixed system and a high mixed liquor suspended solids concentration in the activated sludge were recommended in the report which was the original design basis of this plant. (1)

Another notable design parameter mentioned in this report is temperature where it was recommended that the system be operated at about 85°F.

It becomes evident from an examination of the preliminary design report for this plant (2) and the subsequent review of the final design by the OWRC Division of Sanitary Engineering (3), that these parameters, although considered, were disregarded in the final design of the facilities. It is evident from the graph of final effluent quality for the period March, 1966, to February, 1968, on page 31, that during the winter the efficiency of the sewage treatment plant decreases markedly. This may

ELMIRA WPCP - FINAL EFFLUENT (WEEKLY AVERAGES)



be due to the low temperature. Consideration is now being given to raising the temperature of the raw sewage by the use of waste heat from the Uniroyal (1966) Limited plant. It is also clear from the graph that the effluent quality of the Elmira WPCP is seldom compatible with OWRC objectives. Performance during the summer months is relatively good, but the consistently bad effluent from the plant for up to nine months of the year must raise serious doubts as to the ability of the facilities to ever successfully treat the combined industrial and municipal waste flow. It may, therefore, be worthwhile for the Commission, the Town of Elmira and Uniroyal (1966) Limited to review the alternatives to the joint treatment project in the light of the past three years operating experience.

Treatability and Toxicity Studies

The objectives of this series of investigations are to identify the most toxic and least biologically treatable waste streams from the Uniroyal plant, with a view to the elimination of these wastes from the combined discharge to the Water Pollution Control Plant or the institution of pretreatment measures to render them treatable and non-toxic.

At the beginning of these investigations, it was decided that bio-assays, involving fish toxicity tests, would be used as the measure of the toxicity of wastewater samples. The relationship between this data and the observed toxic effects in Canagagigue Creek has not been clearly established, although it appears reasonable to assume that samples which are markedly toxic to fish will exhibit some degree of toxicity to other aquatic organisms and to cattle.

Initially, samples of Canagagigue Creek above and below the sewage treatment plant effluent and samples of various compnent waste streams from the Uniroyal (1966) Limited plant were tested. This

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established that Canagagigue Creek was significantly toxic to fish below the sewage treatment plant and that this toxicity was not attributable to lack of dissolved oxygen in the creek (see Appendix I). With regard to the toxicity of the in-plant waste samples, it was found that wastes from the manufacture of Flexzones, the Dithiocarbamate and Thiazole wastes and wastes from 2,4,5-Trichlorophenoxyacetic acid production were the most toxic to fish (see Appendices I and III).

However, it is evident that the toxicity of the wastes after passage through the sewage treatment plant is of major significance in relation to conditions in Canagagigue Creek, assuming that all contaminated wastes are discharged to the WPCP. It was, therefore, decided to investigate this aspect of the toxicity problem by conducting biological treatment of the in-plant waste samples independantly and then testing these treated samples for toxicity.

It is at this stage that the current series of investigations have reached. Biological treatment of flexzone wastes, the wastes from the Building 8 sump and thiazole and dithiocarbamate wastes have been carried out and toxicity tests conducted on the treated samples. The Building No. 8 sample proved to be readily treatable and non-toxic after treatment. The flexzone waste is biologically treatable after pH adjustment (see Appendix V), although the treated waste is still toxic, but less so than the untreated waste (see Appendix IV). Biological treatment tends to introduce interfering factors into the toxicity tests from the raw sewage feed (see Appendices II and IV). The elimination of these factors was investigated in further studies conducted in February and March, 1968. Samples of Building No. 8 sump, containing flexzone wastes and the general

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waste sump, containing wastes from MBT and ADAM manufacture were biologically treated and the effluents aerated until the free ammonia content was reduced to a non-toxic level. These treated samples were then submitted for bio-assay. The results of these tests indicate that both samples were readily treatable (see Appendix VI) and that the effluents were almost non-toxic (see Appendix VIII).

Thus, on this basis, it appears that approximately 80 per cent (the total waste flow from the Building No. 8 sump and the general waste sump) of the Uniroyal (1966) Limited wastes are treatable biologically and non-toxic after treatment. However, it must be emphasized that these studies have been conducted in the laboratory with uniform wastes under ideal conditions of temperature, mixing, etc. which bear little relationship to the conditions prevailing at the Elmira Water Pollution Control Plant. Here; the wastes are highly variable and during the winter, often close to freezing.

The degree to which temperature affects biological treatment of these wastes is now being investigated by the Division of Research and by Uniroyal (1966) Limited. It is expected that measures will be taken to raise the temperature of the wastes during the winter months.

In addition, it is evident from the previous discussion of the equalization capacity of the waste holding lagoons that measures are necessary to reduce the wide fluctuations in the strength of wastes discharged from this system. Recirculation of the lagoon effluent is being considered as a solution to this problem.

Information available in the literature (4) on the toxicity of some of the compounds manufactured in the Elmira plant by Uniroyal (1966) Limited suggest that certain wastes may be significantly toxic to fish and animals even when only trace levels of the compounds are present.

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Table V summarizes the toxicity data for these compounds.

TABLE V

Toxicity of Certain Uniroyal Compounds

Compound		Toxicity to Animals	Toxicity to fish
TUEX Tetra methyl thiuram disulphide	Rats:	LD_{50} = 350 mg/kg or 865 mg/kg	Catfish fingerlings 96 hrTL_M = 0.79 ppm at 19°C.
	Rabbits:	LD = 350 mg/kg	
Methyl ADAM Dimethyl dithiocarbamate	Rats:	LD_{50} = 800 mg/kg	1 ppm fatal to guppies after 30 hrs. at 21°C.
	Mice:	LD_{50} = 285 mg/kg	
METHAZATE Zinc dimethyl dithiocarbamate		--------------	Fat head minnows 96 hr. TL_M = 0.008 ppm in soft water.
2,4,-D 2,4,-dichloro phenoxy acetic acid	Rats:	LD_{50} = 666 mg/kg	Bass and bluegills 24hr. TL_M = 350 mg/l Ester and amine derivatives more toxic, 1-5 ppm of butyl ester caused 40-100% mortality to bluegills.
	Mice:	LD_{50} = 375 mg/kg	
	Rabbits:	LD_{50} = 800 mg/kg	
	Dogs:	LD_{50} = 100 mg/kg	
2,4,5-T 2,5,trichloro phenoxy acetic acid	Rats:	LD_{50} = 300 mg/kg	Threshold toxicity for perch = 55 mg/l and for bleak = 60 mg/l

N.B. LD_{50} = Lethal dose required to produce 50% mortality, expressed in mg/kg body weight.

TL_M = Median tolerance limit, concentration required to produce 50% mortality.

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There is little information available on the effects of these and other Uniroyal (1966) Limited products on sewage treatment processes, or conversely, on the effects of biological treatment on the toxicity of these products. There is some suggestion (5) that amino-triazole compounds are not measurably degraded biologically and that such compounds inhibit biological treatment processes.

On the basis of a biological survey of Canagagigue Creek, there is evidence to suggest that the discharge from the sewage treatment plant is not the only source of toxic pollutants in the creek; the line of demarcation between a normal and an abnormal biological community in the creek was found to be some distance upstream from the sewage treatment plant outfall. This is clearly demonstrated by Figure I on page 37, which is an extract from the Grand River survey report. Possible sources of contamination above the sewage treatment plant effluent are the cooling water discharges, seepage of strong wastes from the lagoons and seepage from waste pits located a short distance from the east bank of the creek (see diagram on page 12).

The cooling water discharges from this plant, as has been previously discussed, do not appear to be significant sources of contamination, although traces of contaminants are present in these discharges.

Soil characteristics in the general area of the plant are of a coarse gravel type. This suggests that seepage from the lagoons and the waste pits could occur quite readily if no attempt was made to use non-permeable materials, such as clay, in the construction of these facilities. The waste pits are located some distance above the level of the creek, which would tend to encourage seepage from the pits to travel towards the creek. In addition, the waste storage lagoons were originally

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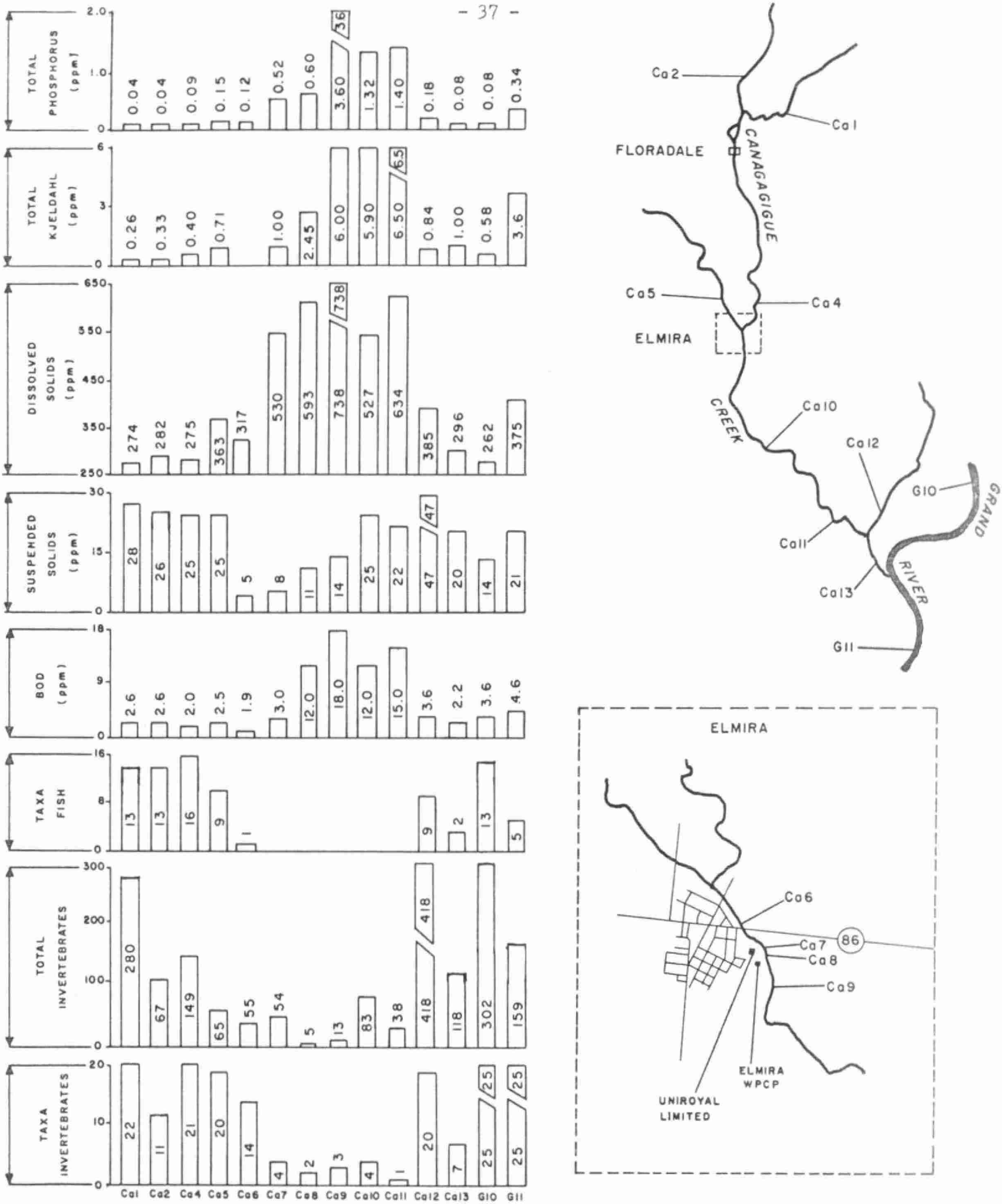

FIG. 1 BIOLOGICAL AND CHEMICAL CONDITIONS AT 15 STATIONS ON THE CANAGAGIGUE CREEK - GRAND RIVER IN JUNE, 1966.

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constructed by diverting the creek around the south end of the plant property and the sewage treatment plant. The embankment material of the lagoons is, therefore, partly constructed from coarse gravel from the original creek bed. This material would likely encourage the seepage of strong wastes from the lagoons to the creek.

Improved treatment efficiency at the sewage treatment plant is essential regardless of whether seepage or other factors are significant sources of the toxicity problem in the creek. Toxicity tests on the sewage treatment plant effluent indicate that it is significantly toxic, even when effluent quality approaches OWRC objectives (see Appendix IV, sample BY 113, laboratory number T-2555). At this stage, it is not known whether this toxicity is due to the passage of non-biodegradable toxic components through the sewage treatment plant or due to the presence of toxic degradation products of the biological treatment processes. It is doubtful that such a differentiation of the source and nature of the toxicity will be made, in view of the complex nature of the wastes and the difficulties involved in obtaining chemical analytical data. However, it is evident that if improved treatment efficiency at the sewage treatment plant and the pretreatment or elimination of the most toxic waste streams from the Uniroyal (1966) Limited plant fail to reduce the toxicity of the sewage treatment plant effluent to acceptable levels, consideration must be given to advanced waste treatment processes or to alternatives to biological treatment for these wastes. Furthermore, the provision of an acceptable level of toxicity to fish does not necessarily mean that the toxicity to other aquatic organisms, or higher animals, has been eliminated or that adverse effects due to prolonged exposure to low levels of toxicity may not occur.

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It is clear, therefore, that no quick solution to this problem is likely to be forthcoming. The current series of investigations into the toxicity and treatability of the Uniroyal (1966) Limited wastes will be continued to the point where the most toxic waste streams have been identified and consideration can be given to alternative disposal or pretreatment of these waste streams. However, work conducted to date suggests that under laboratory conditions biological treatment can render most of these wastes non-toxic. It, therefore, remains to be seen whether the treatment achieved in the laboratory can be duplicated at the Elmira Water Pollution Control Plant.

CONCLUSIONS AND RECOMMENDATIONS

It is evident from the results of this survey and the numerous investigations carried out by other OWRC Divisions over the past three years, that this is one of the outstanding pollution problems in the Province. The present condition of Canagagigue Creek, the past history of cattle mortality attributable to the use of the creek for watering cattle and the continued inability of the Elmira Water Pollution Control Plant to continuously produce an acceptable effluent all bear witness to this fact.

The wastes resulting from operations at the Uniroyal (1966) Limited plant are complex, toxic, variable and, consequently, difficult to treat biologically. The treatability aspect of this problem is the subject of continuing investigations by the Technical Advisory Services Branch of the OWRC Division of Research. Tentative conclusions from these studies are that most of the Uniroyal wastes (80%) are treatable biologically under laboratory conditions. It remains to be seen whether laboratory conditions can be duplicated at the Elmira WPCP.

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Major difficulties at the WPCP appear to be centred around the seasonal deterioration in effluent quality, brought about by low temperatures during the winter months, and process upsets brought about by extreme variations in waste strength and/or toxicity.

It is, therefore, recommended that measures to raise the temperature of the wastes be investigated and instituted before the winter of 1968. It is also recommended that consideration be given to improving the equalization capacity of the lagoon system, such as by the installation of baffles or by the recirculation of part of the lagoon effluent back to the inlet.

With regard to process upsets at the WPCP caused by batch discharges of high strength or toxic wastes, it is expected that improved waste equalization will reduce these problems. However, with respect to the most recent incident, in February, 1968, it is recommended that high strength cyanide wastes from MONEX production be tested for cyanide and if necessary treated by alkaline chlorination prior to disposal to the lagoon system.

It is not known to what extent improved treatment efficiency in the WPCP will reduce the toxicity of the effluent. Bio-assay and treatability studies conducted to date indicate that substantial reductions in the toxicity of the Uniroyal wastes result from biological treatment. Conversely, the toxicity of the WPCP effluent during periods of good treatment efficiency suggest that these facilities may be inadequate to reduce toxicity to acceptable levels.

It, therefore, remains to be seen whether improved treatment efficiency at the sewage treatment plant can control the toxicity problem.

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In the event that such control cannot be achieved with the existing facilities, advanced waste treatment processes may be necessary. At this stage, it must be recognized that the costs of advanced waste treatment may dictate an examination by all parties concerned of the alternatives to the treatment of the wastes from the Uniroyal (1966) Limited plant in the Elmira Water Pollution Control Plant.

It is evident from the biological survey of the Canagagigue Creek conducted by the OWRC Biology Branch, that the effluent from the sewage treatment plant is not the only source of toxic components in the creek. Other possible sources of contamination are seepage from the lagoons and/or waste pits and inadvertent discharges of strong wastes directly to the creek via the cooling water disposal system. The most likely source would appear to be seepage from the lagoon system and it is, therefore, recommended that measures to reduce seepage, such as by lining the lagoons with plastic sheet or other impervious material, be instituted by the Company.

The overall nature of the problem is such that the conventional parameters of pollution, such as BOD, COD and suspended solids, are inadequate. The absence of significant biota in the creek, the operating problems at the WPCP and the toxicity of the effluent cannot be related adequately to these parameters. In the absence of analytical data on specific compounds which can be related to the adverse conditions in the creek and at the WPCP, some measure of total organic content, such as total organic carbon, should provide additional useful data relating to the gross efficiency of removal of organics through the WPCP. It is recommended that total organic carbon be considered as an analytical tool in future studies at this plant.

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In view of the known pollutional characteristics of boiler blowdown, it is recommended that the discharge of this waste to the creek be discontinued and the waste be directed to the Elmira WPCP.

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REFERENCES

1. "Design Criteria for Biological Treatment of 2,4,-D and Chemical Plant Effluent" by R. E. Mills of Naugatuck Chemicals, Division of the Dominion Rubber Company Limited. Presented at the 16th Purdue Industrial Waste Conference, 1961.

2. Report on Trade Waste Disposal at Naugatuck Chemicals, Elmira by Canadian British Engineering Consultants, December, 1961.

3. Sewage Treatment Plant Check Sheet, Division of Sanitary Engineering, June, 1963.

4. "Water Quality Criteria" 2nd edition by McKee and Wolf, The Resources Agency of California, State Water Quality Control Board.

5. "Behaviour of 3-Amino-1,2,4,-Triazole in Surface Water and Sewage Treatment" by F. S. Ludzack and J. W. Mandia.

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A P P E N D I X I

Inter-Office Memorandum

Date: November 23, 1966.

To:	From:
Mr. K. Shikaze,	Miss Y. H. Swabey,
Division of Industrial Wastes.	Biology Branch.

Re: NAUGATUCK CHEMICAL CO., ELMIRA

Samples of various wastes collected from the Naugatuck Chemical Company, Elmira, on November 3, 1966, were received by the Biology Branch for bio-assay as follows:

Biology No.	Sampling Point
B 2993	2,4,5-T Acid wastes
2994	Elmira WPCP effluent
2995	Building 28 Sump
2996	Skimmer pond
2997	Building 8 Sump
2998	2,4,-D waste pit
2999	Naugatuck waste after pretreatment
Received on November 14, 1966:	
B 3028	Building 28 - Flexzone wastes

Since an insufficient number of acclimated minnows were on hand for seven samples on November 7, preliminary tests were run using guppies (Lebistes reticulatus). For these tests 500-ml volumes of various concentrations of the wastes were prepared with Toronto tap water as diluent. Guppies were exposed for 24 hours at room temperature (approx. 21°C). The pH of the highest concentrations was determined at the beginning of the test.

Results of these tests are given in Table I, where 0 indicates no mortality and the figures represent the number of hours in which 100 per cent mortality occurred.

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On November 14, tests were run on samples 2993 - 2999 and on 3028 using fathead minnows (Pimephales promelas) in 2-litre volumes. The pH of each solution was determined at 0 and 24 hours. D.O.s were determined where indicated and where colour of the solution permitted. The tests were terminated at 48 hours.

Results of these tests are given in Table 2 where, as before, the mortality figures are the number of hours in which 100 per cent mortality occurred. There was no mortality in the four controls set up in Toronto tap water. Chemical data obtained during the tests with minnows are given in Table 3.

The tests on guppies were useful in determining the range of concentrations in which to test the minnows. It will be noted by comparing Tables 1 and 2, however, that the minnows often died in lower concentrations (Samples 2993, 2995, 2997 and 2998). This is not unusual considering the differences in sensitivity among fish species. Data are available which show that guppies are less sensitive to a mixture of 2,4,-D and 2,4,5-T than at least two other species of fish.

In two instances the guppies exhibited more sensitivity than the minnows: Sample 2994, 50 per cent, and Sample 2999, 1 per cent. Four possibilities have occurred to me regarding this difference:

(1) The guppies died from lack of oxygen in 2994.

(2) Both samples detoxified during one week of cold storage.

(3) Toxicity was influenced by the size of the fish in relation to the volume of toxicant.

(4) The minnows changed the chemical composition of the 50 per cent solution of 2994 and the 1 per cent 2999.

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Although the D.O. was not determined in the 50 per cent solution of 2994, I believe it highly unlikely that it was sufficiently low to kill the guppies in 2 hours.

Secondly, all samples could have changed chemically during storage, but the mortality of 2993 - 10 per cent and 2995 - 10 per cent were similar in both guppy and minnow tests. Moreover, the pH of the high concentrations of the wastes was the same in both tests. It is questionable therefore, whether the samples changed during this time.

It is possible that the amount of toxicant present in relation to the size of the fish influenced the results obtained. The minnows were exposed to a solution volume of 1.1 litre per gram of fish while the guppies were placed in the equivalent of 10 litres per gram of fish. Studies on insecticides have indicated that toxicity can increase with increasing volume of toxicant, to a point.

The different sizes of the fish could have been a factor also if the chemical composition of the wastes was changed by the presence of the minnows. It has been demonstrated that the presnce of bluegills in a solution of 4(2,4-dichlorophenoxybutyric) acid can convert this material to 2,4,-D. It could have been possible, therefore, for the minnows to convert this or similar substances present in the 2,4,-D waste (2999). If the conversion products were less toxic than the original materials, it would explain why the guppies died in a 1.0 per cent concentration and the minnows did not. The conversion of 4(2,4,-DB) to 2,4,-D results in detoxification, since the 24-hr. TLm for the former (dimethylamine salt, with bluegills) is 10 ppm, whereas the TLm for 2,4,-D (DMS) is 350 ppm.

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Regarding the relative toxicity of the wastes to minnows, Samples 2993 (2,4,5-T), 2995 (Bldg. 28 sump) and 3028 (Flexzone) seem to be the most toxic. The first two were lethal at 1.0 per cent, the other at 0.1 per cent. The toxicity of 3028 may have been influenced by high pH, and I shall run some tests to ascertain this. Certain other mortalities in the tests could have been caused by low pH: in the 10.0 per cent concentrations of 2995 and 2996 and the 50 per cent solution of 2997.

In conclusion, I would suggest that we proceed as follows:

(1) Run full-scale tests on 2993, 2995 and 3028.

(2) Check the range of 2994 and 2999, using fresh samples, on minnows.

(3) Determine the upper lethal limit of pH for fathead minnows under our test conditions.

For these tests, I would require the following volumes of samples:

2993)
2995)
3028) 40 oz. each
2999)

2994 - 1/2 gallon

If you are agreeable to this procedure, please discuss with me the timing of the tests so that I can make appropriate arrangements.

Original signed by

Y. H. Swabey

TABLE I

Mortality of guppies in Naugatuck wastes

	Concentration, % by volume			
Sample	.1	1.0	10.0	50.0
2993	0	0	1.5	-
pH	-	-	8.0	-
2994	-	0	0	2
pH	-	-	-	7.3
2995	0	0	1	-
pH	-	7.0	2.9	-
2996	0	0	5	-
pH	-	7.1	4.9	-
2997	0	0	0	-
pH	-	-	6.1	-
2998	0	0	-	-
pH	-	7.7	-	-
2999	0	22*	22	-
pH	-	-	7.6	-

* 40% mortality

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TABLE II

Mortality of minnows in Naugatuck wastes
(Number of hours for 100% mortality).

Sample	Concentration, % by volume .01	.1	1.0	10.0	50.0
2993	-	0	8.5	1.5	-
2994	-	-	0	0	21
2995	-	0	11	1.5	-
2996	-	0	0	2.5	-
2997	-	-	0	20.5	1.5
2998	-	-	0	1.5	1.5
2999	-	0	0	23	-
3028	0	9	4.5	1.5	-

TABLE III

Chemical data from minnows tests.

Sample		Concentration, % by volume .01		.1		1.0		10.0		50.0	
2993	pH	-		7.6	7.9	7.6	7.9	8.3	8.3	-	
	D.O.	-		-		6.4	7.2	8.0	8.0	-	
2994	pH	-		-		7.7	7.6	7.7	7.6	7.3	7.6
	D.O.	-		-		-		6.8	5.0	-	
2995	pH	-		7.6	7.5	7.3	7.6	3.0	3.0	-	
	D.O.	-		-		7.8	8.0	-		-	
2996	pH	-		7.5	7.4	7.1	7.3	4.9	5.1	-	
	D.O.	-		-		7.6	7.6	-		-	
2997	pH	-		-		7.4	7.5	6.2	6.9	3.5	3.5
	D.O.	-		-		-	5.6	-		-	
2998	pH	-				7.8	7.5	8.5	7.9	8.8	8.4
	D.O.	-				7.6	6.2	-		-	
2999	pH	-		8.2	7.7	8.1	7.6	7.9	7.4	-	
	D.O.	-		7.0	-	-	6.0	-		-	
3028	pH	8.3	8.1	9.1	8.6	11.0	10.4	12.5	12.4		
	D.O.	-		7.4	6.6	-		-		-	

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APPENDIX II

Inter-Office Memorandum

Date: March 20, 1967.

To:	From:
Mr. K. Shikaze,	Miss Y. H. Swabey,
Division of Industrial Wastes.	Biology Branch.

Re: UNIROYAL, ELMIRA - BIO-ASSAYS, JANUARY - FEBRUARY, 1967

The following samples were received by the Biology Branch for bio-assay during January and February:

Date	Sample No.	Source	Tested
Jan. 10	BY 1	Elmira town sewage	Jan. 10
	BY 2	Elmira WPCP final effluent	"
	BY 3	Uniroyal Bldg. 28 sump	"
	BY 4	Uniroyal Flexzone waste	Jan. 10, 12, Feb. 7
Feb. 9	BY 9	Elmira WPCP effluent	Feb. 15
	BY 10	WPCP effluent, treatment 1	"
	BY 11	" 2	"
	BY 12	" 3	"
	BY 13	" 4	"
Feb. 22	BY 17	Uniroyal Bldg. 8 waste, biological oxidation	Feb. 28
	BY 18	Uniroyal Bldg. 8 waste, (control)	"

Fish used in all bio-assays on these samples were fathead minnows (Pimephales promelas). Tests were run at ambient temperature (about 21°C) and aged Toronto tap water was used as diluent. All samples except 3 and 4 were prepared in 2-liter volumes in 1-gallon jars. Samples 3 and 4 were set up in 10-liter volumes in 5-gallon jars.

The results of the bio-assays are given in the accompanying tables.

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TABLE 1 Bio-assay results, Samples 1, 2 and 3

The samples of town sewage and WPCP effluent (not chlorinated) were aerated for one day to reduce the oxygen demand and solutions were aerated during the tests. Azide Winkler determinations indicated satisfactory levels of D.O. except in the 50 per cent WPCP effluent at 24 hours. Fish mortality in both Samples 1 and 2 can be attributed mostly to ammonia with perhaps some contribution by ABS. The town sewage contained 24.6 ppm free ammonia as N and 2.3 ppm ABS. The WPCP effluent contained 23.0 ppm ammonia and 4.3 ppm ABS. Unfortunately, these normal constituents of sewage can mask any effects of other toxicants.

Forty per cent mortality occurred in the .1 per cent solution of Bldg. 28 sump waste. Since no mortality occurred at this concentration of a previous sample (see memo dated November 23, 1966), the fish used in the January 10 test were apparently hypersensitive. This is borne out by the results of repeated tests on Sample 4 (Flexzone waste) detailed in Table 2.

TABLE 2 Bio-assay results, Sample 4, Flexzone raw waste and neutralized

TABLE 3 Chemical data from Flexzone waste bio-assays

Fish died in the .01 per cent concentration of the raw waste prepared on January 10, whereas no mortality occurred at this concentration during the test last fall. Additional tests, set up on January 12 and February 7, indicate that .01 per cent should not be toxic within 24 hours. In all tests, the neutralized waste was only slightly less toxic than the raw waste. Twenty-four hour median tolerance limits (TLm) determined from the February 7 data were .015 per cent for the raw waste, .024 per cent for the neutralized waste. The chemical data in Table 3 indicate that oxygen levels were satisfactory.

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TABLE 4 Results of bio-assays on samples of WPCP effluent treated various ways (Samples 9 - 13)

These samples were aerated for two days and solutions aerated during testing. Nevertheless, oxygen levels were low in the 25 and 50 per cent solutions of sample 11 and lethal in the 50 per cent concentration of Sample 9. The ammonia content of these samples was not determined. Samples 10 and 12 (Treatments 1 and 3) smelled strongly of chlorine and it was learned from Mr. Ross Mills via Mr. R. Abbott that these did indeed have a high residual chlorine content. The odour of chlorine was still present after two days aeration and results of analysis by Chemistry Branch personnel (included in Table 4) indicated 30 ppm chlorine in the 50 per cent concentration of both samples. Sodium thiosulphate was added to one of the duplicate solutions of each concentration and controls in amounts calculated to eliminate the chlorine. These amounts would not have been toxic to fish. Evidently insufficient thiosulphate was added, since fish died quickly in the 50 per cent concentration of both samples. Further analyses showed chlorine residuals of 2.00 and 3.75 ppm in these solutions. Mortalities in Treatments 1 and 3 samples can therefore be attributed to chlorine.

There was least mortality in solutions of Sample 13 (Treatment 4). Seventy-five per cent of the fish died in the 50 per cent concentration in 24 hours, 100 per cent in 25 hours.

While the Treatment of 4 sample appeared to be least toxic of this group, the oxygen demand of the untreated waste and Treatment 2 sample prevented a valid comparison of toxicity.

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TABLE 5 Results of bio-assays on Building 8 waste

The results of tests on two samples of Building 8 waste delivered to Biology by Mr. Mills were outlined in a letter to him on March 2 (copy to Industrial Wastes). The sample of raw waste was non-toxic in concentrations up to 50 per cent. That treated by biological oxidation caused death at 25 per cent. Although the samples were aerated for two days and tested under constant aeration, and Winkler tests indicated satisfactory D.O. levels, obvious interference with the Winklers on the treated sample suggested that the D.O. figures may have been invalid. The cause of death in the treated sample cannot be stated with any certainty.

Comment

WPCP effluents are extremely difficult to evaluate for toxicity due to their oxygen demand. If this is overcome, the characteristic ammonia and ABS concentrations can be sufficiently high to mask effects of other possible toxicants. Any reduction which can be made in the oxygen demand of such effluent samples would greatly facilitate any future tests, (A D.O. meter to provide more reliable data on complex wastes is on order).

Similarly, treatments of WPCP effluents designed to reduce toxicity cannot be properly evaluated when the treatment involves the introduction of acutely toxic materials. If at all possible, such materials should be eliminated from samples before they are submitted.

Original signed by,

Y. H. Swabey

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TABLE 1

Bio-assay results, Samples 1, 2 and 3.

Sample	Conc'n, %	% Mortality, 24 hr.	D.O., ppm 0 hr.	D.O., ppm 24 hr.	pH 0 hr.	pH 24 hr.
1. Town sewage	0	0	7.76	-	8.3	8.2
	10	0	6.00	-	8.3	8.2
	25	100	6.56	7.20	8.3	8.5
	50	100	7.74	7.36	8.2	8.6
2. WPCP eff.	0	0	7.84	-	8.3	8.2
	10	0	7.68	-	8.2	8.2
	25	50	7.40	7.04	8.2	8.3
	50	100	7.22	3.76	8.3	8.3
3. Bldg. 28 sump	0	0	8.16	-	7.8	7.7
	.1	40	7.96	5.90	7.9	7.7
	.18	100	8.04	-	8.2	8.3
	.32	100	7.96	-	8.7	8.7
	.56	100	7.60	-	9.0	9.0
	1.0	100	7.90	-	9.6	9.3

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TABLE 2

Bio-assay results, Sample 4, Flexzone raw waste and neutralized

Conc'n %	% Mortality, 24 hr. Jan. 10	Jan. 12	Feb. 7
Raw Waste			
0	20	0	0
0	-	-	0
.0032	-	0	-
.0032	-	-	-
.0056	-	0	0
.0056	-	-	0
.01	100	0	0
.01	-	-	0
.018	100	40	60
.018	-	-	80
.032	100	-	100
.032	-	-	100
.056	100	-	-
Neutralized Waste			
0	0	0	0
0	-	-	0
.01	-	0	0
.01	-	-	0
.018	40	0	0
.018	-	-	0
.032	100	40	100
.032	-	-	100
.056	100	-	100
.056	-	-	100
.1	100	-	-
.18	100	-	-

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TABLE 3

Chemical data from Flexzone waste bio-assays

Date	Conc'n	Raw Waste D.O. ppm 0 hrs.	Raw Waste D.O. ppm 24 hrs.	Raw Waste pH 0 hrs.	Raw Waste pH 24 hrs.	Neutralized Waste D.O. ppm 0 hrs.	Neutralized Waste D.O. ppm 24 hrs.	Neutralized Waste pH 0 hrs.	Neutralized Waste pH 24 hrs.
Jan. 10	0	7.98	6.42	7.8	7.7	8.54	-	8.2	7.9
	.01	8.10	7.62	4.4	8.4	-	-	-	-
	.018	8.26	-	8.5	8.4	8.54	6.30	8.0	7.9
	.032	7.92	-	8.7	8.6	8.46	-	8.1	7.8
	.056	8.16	-	9.2	9.0	8.00	-	7.9	7.8
	.1	-	-	-	-	8.22	-	7.9	7.9
	.18	-	-	-	-	7.60	-	7.9	8.0
Jan. 12	0	7.66	-	7.8	7.7	7.98	-	8.1	7.6
	.0032	7.76	-	7.8	7.6	-	-	-	-
	.0056	8.04	-	8.1	7.4	-	-	-	-
	.01	8.02	-	8.2	7.5	7.72	-	7.9	7.5
	.018	8.14	6.86	8.5	7.7	8.12	-	7.9	7.5
	.032	-	-	-	-	7.78	6.00	7.9	7.7
Feb. 7	0	7.6	6.8	8.0	7.8	7.6	6.0	8.1	7.6
	.0056	7.8	7.0	8.2	7.8	-	-	-	-
	.01	7.6	6.6	8.4	7.6	7.6	6.8	7.9	7.6
	.018	7.6	6.4	8.5	7.9	7.8	6.2	8.1	7.6
	.032	7.4	-	8.7	-	7.8	-	8.2	-
	.056	-	-	-	-	7.8	-	8.1	-

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TABLE 4

Results of bio-assays on samples of

WPCP effluent treated various ways (Samples 9 - 13)

Sample	Conc'n %	% Mortality in-hr.	D.O. ppm 0 hr.	D.O. ppm 24 hr.	pH 0 hr.	pH 24 hr.	Cl ppm 0 hr.
9. WPCP eff.	0	25 in 9 hr.	-	6.0	7.8	7.6	-
	10	0 " 24	4.76	4.6	7.7	7.5	0
	25	100 " 2	0.92	-	7.7	-	-
	50	100 " .5 hr.	-	-	7.9	-	-
10. Treatment 1	0	0 " 24 hr.	-	6.4	8.1	-	-
	10	100 " 1	8.64	-	8.3	-	6.0
	25	100 " .5	-	-	8.3	-	15.5
	50	100 " .3	-	-	8.3	-	30.0
10. Treatment 1 (+thiosulphate)	0	0 " 24 hr.	-	4.2	8.2	7.6	-
	10	0 " 24	6.78	6.2	8.1	7.7	-
	25	100 " 2.3	5.58	-	7.9	-	-
	50	100 " 1.3	-	-	7.7	-	3.75
11. Treatment 2	0	0 " 24 hr.	-	6.0	8.1	7.6	-
	10	0 " 24	-	6.0	7.9	8.0	-
	25	25 " 8	3.74	3.8	7.9	7.7	-
	50	100 " 9	2.46	-	7.9	-	-
12. Treatment 3	0	0 " 24 hr.	-	5.6	8.1	-	-
	10	100 " .75	8.82	-	8.2	-	5.5
	25	100 " .3	-	-	8.3	-	18.0
	50	100 " .3	-	-	8.4	-	30.0
12. Treatment 3 + thiosulphate	0	0 " 24 hr.	-	4.4	8.1	-	-
	10	100 " 19	4.54	-	8.0	-	-
	25	100 " 19	-	-	8.0	-	-
	50	100 " 2	-	-	8.0	-	2.00
13. Treatment 4	0	0 " 25	-	6.4	8.1	7.7	-
	10	0 " 25	-	6.6	8.2	7.9	-
	25	0 " 25	6.36	5.2	8.4	8.0	-
	50	100 " 25	5.68	5.0	8.6	8.2	-

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TABLE 5

Results of bio-assays on Building 8 waste

Sample	Conc'n %	% Mortality			D.O., ppm 0 hr.	D.O., ppm 24 hr.	pH 0 hr.	pH 24 hr.
17. Bldg. 8 waste, biol. oxid.	0	0	in	24 hr.	9.90	7.80	-	8.2
	10	0	"	"	8.70	7.90	-	8.0
	25	100	"	7 hr.	8.86	4.56	-	7.8
	50	100	"	1.5 hr.	8.76	4.34	7.6	7.8
18. Bldg. 8 waste	0	0	"	24 hr.	8.76	8.26	-	8.1
	10	0	"	"	10.04	7.90	-	8.1
	25	0	"	"	7.90	7.58	-	8.1
	50	0	"	"	4.30	7.38	7.5	7.9

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APPENDIX III

Inter-Office Memorandum

Date: April 12, 1967.

To:	From:
Mr. K. Shikaze,	Miss Y. Swabey,
Division of Industrial Wastes.	Biology Branch.

Re: BIO-ASSAY OF UNIROYAL WASTES, MARCH 29, 1967

One-gallon samples of the following wastes were delivered to the laboratory by Mr. R. E. Mills, Uniroyal Ltd., on March 28, 1967:

Sender's No.	Biology No.	Description
1	BY 33	Dithiocarbamate and thiazole wastes
2	BY 34	Sample 1 plus biological oxidation
3	BY 35	Sample 1 air-stripped
4	BY 36	Sample 3 plus biological oxidation
5	BY 37	Building 8 raw waste
6	BY 38	Sample 5 plus biological oxidation

All samples were aerated at room temperature from 2:30 p.m. March 28 to 10:30 a.m. March 29. Various dilutions were then prepared in 2-liter volumes with aged Toronto tap water. Fathead minnows (Pimephales promelas) were exposed to the dilutions for 24 hours at room temperature. Samples 1, 3, 4 and 5 were aerated during the test.

Results of the bio-assays are given in Table 1, attached. Biological oxidation did not reduce the toxicity of the dithiocarbamate and thiazole wastes (sample 1) appreciably. Sample 1 was toxic at 10 per cent, sample 2 at 25 per cent. The air-stripped waste, sample 3, was toxic at 10 per cent, but this mortality can be attributed to lack of oxygen.

Oxygen levels were satisfactory in dilutions of sample 4, which was toxic at 25 per cent, non-toxic at 10 per cent. Mortality in the

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Building 8 waste (Sample 5) was attributable to D.O. lack, so that the non-toxicity of the biologically oxidated waste (Sample 6) cannot be compared validly with it.

Original signed by,

Y. Swabey

TABLE 1

Results of bio-assays on Uniroyal samples, March 29, 1967

Sample	Conc'n %	% Mortality	D.O. ppm 0 hr.	24 hr.	pH
1	0	0 in 24 hr.	-	-	8.1
	1	0 24	-	-	
	10	100 1.5	6.68	-	7.6
	25	100 .5	-	-	8.4
	50	100 .25	-	-	8.7
2	0	0 in 24 hr.	-		7.8
	10	0 24	-	5.64	8.0
	25	100 16.5	5.90	4.80	7.9
	50	100 13.5	5.62	-	7.9
3	0	0 in 24 hr.			8.0
	1	0 24	8.40	6.30	7.9
	10	100 1.5	3.50	-	7.3
	25	100 1.5	-	-	7.3
	50	100 .25	-	-	7.9
4	0	0 in 24 hr.	-	-	8.0
	10	0 24	7.60	-	8.1
	25	100 16.5	6.76	7.50	7.0
	50	100 15.5	6.12	-	6.2
5	0	0 in 24 hr.	-	-	7.9
	10	0 24	-	-	7.8
	25	100 18.5	5.15	0.60	7.7
	50	100 1.5	3.76	-	7.3
6	0	0 in 24 hr.	-	-	7.9
	10	0 24	-	-	7.6
	25	0 24	-	-	8.1
	50	0 24	7.14	-	8.4

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APPENDIX IV

Inter-Office Memorandum

Date: October 20, 1967.

To:	From:
Mr. R. A. Abbott,	Mrs. Y. Lambert,
Division of Industrial Wastes.	Biology Branch.

Re: UNIROYAL, LTD., ELMIRA - SUMMARY OF BIO-ASSAYS JUNE THROUGH SEPTEMBER, 1967

The following samples were received by the Biology Branch for bio-assay:

Biology No.	Date Received	Description
BY 88	June 28	Flexzone waste 3% biological oxidation OWRC
BY 92	July 4	Building 8 waste, biological oxidation OWRC
BY 93	July 4	Flexzone waste 3% biolobical oxidation OWRC
BY 93A	July 6	Flexzone waste 3% biological oxidation OWRC
BY 113	Aug. 4	Elmira STP effluent
BY 157	Sept. 18	Flexzone waste 3% biological oxidation OWRC

Range tests were performed on Samples 88, 92, 93 and 113; full-scale tests on Samples 93A and 157. For the range tests, two fish were exposed to 2-litre volumes of various concentrations in 1-gallon jars with aged Toronto tap water as diluent. Five fish per 10-litres in 5-gallon jars were used in the full-scale tests. All fish were fathead minnows (<u>Pimephales promelas</u>) which had been acclimated to laboratory conditions. Bio-assays were run at ambient temperature, about 21°C. Tests were terminated at 24 hours.

Results of the bio-assays and the chemical data obtained concurrently are given in Tables 1 and 2.

On receipt by the Biology Branch, Sample 88 had a D.O. greater than 7 ppm and a pH over 12. It was neutralized to 6.8 before testing.

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This sample produced mortality at a concentration of 10 per cent within seven hours.

It was understood that Sample 93 consisted of neutralized waste and its high pH was not detected until the range test on it had been set up. Mortality in this test may have been influenced by this. Consequently, a fresh sample (93A) was obtained and this had been neutralized before submission. Sample 93A caused 100 per cent mortality at a concentration of 32 per cent and no mortality at 18 per cent, yielding a 24-hour TLm of 24 per cent. Since the sample was only 3 per cent waste, the TLm of the pure waste could be calculated to be 0.72 per cent, somewhat higher than the .024 per cent TLm previously obtained on neutralized, non-oxidated waste.

The sample of waste received on September 18, (157) evidently had a very high BOD, since the mortality down to 5.6 per cent could be attributed to oxygen lack. This test was not, therefore, a valid test of toxicity.

Building 8 waste (Sample 92) was found to be non-toxic in 24 hours, as was the case with a previous sample.

The sample of Elmira STP effluent received on August 4, caused 100 per cent mortality at a concentration of 50 per cent, but not at 25%, (Table 2). This sample was, therefore, less toxic than the one received February 9, 1967 which was lethal at 25 per cent.

Original signed by,

Y. Lambert

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TABLE 1

RESULTS OF BIO-ASSAYS ON UNIROYAL WASTES

JUNE TO SEPTEMBER, 1967

Sample No.	Conc'n. % by Vol.	% Fish Mortality	D.O. ppm 0 hr.	D.O. ppm 24 hr.	pH 0 hr.	pH 24 hr.
88	10.	100 in 7 hr.	-	-	7.5	-
	1.	0 " 24 hr.	8.62	-	7.7	-
	0.1	0 " "	8.44	-	7.7	-
	0.01	0 " "	7.86	-	7.7	-
	0.00	0 " "	8.04	-	7.7	-
93 (Range)	100	100 in 1.25 hr.	-	-	9.6	9.5
	50	100 " 11 hr.	-	-	9.6	9.5
	25	0 " 24 hr.	-	-	9.4	9.2
	10	0 " "	-	-	9.3	8.4
	1	0 " "	-	-	8.6	8.0
	0	0 " "	-	-	8.3	8.0
93A	56	100 in 24 hr.	7.40	4.18	8.0	8.2
	32	100 " "	6.80	5.52	8.0	8.1
	18	0 " "	7.90	5.00	8.2	8.2
	10	0 " "	7.20	5.46	8.2	8.2
	5.6	0 " "	8.32	5.34	8.3	8.1
	0.0	0 " "	7.58	6.30	8.5	8.1
157	56	100 in 24 hr.	3.00	-	7.4	-
	32	" " "	4.10	0.00	7.5	-
	18	" " "	5.60	0.80	7.85	-
	10	" " "	5.50	3.10	8.05	-
	5.6	" " "	7.50	3.30	8.2	-
	0.0	0 " "	9.30	7.30	8.35	-
92	100	0 in 24 hr.	5.10	-	8.5	-
	50	" " "	-	-	8.5	8.1
	10	" " "	-	-	8.4	8.2
	0	" " "	-	-	8.4	8.5

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TABLE 2

RESULTS OF BIO-ASSAY ON ELMIRA STP EFFLUENT

Sample No.	Conc'n. % by Vol.	% Fish Mortality	D.O. ppm 24 hr.	pH 0 hr.
113	100	100 in 24 hr.	-	-
	50	100 " "	-	-
	25	0 " "	7.16	7.9
	10	0 " "	8.24	7.95
	1	0 " "	-	8.0
	0	0 " "	-	7.85

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APPENDIX V

Inter-Office Memorandum

Date: December 14, 1967.

To:

Central Records

From:

Mr. J. Smart,

Technical Advisory Services.

Re: MODEL SCALE BIOLOGICAL TREATMENT OF NAUGATUCK WASTES: Flexzone and Building 8 General Sump

In the biological treatability studies of the above two wastes, model "Rapid Bloc" type units were used at a waste retention time of fifteen hours.

The Flexzone study can be separated into four phases, namely:

Phase (1)

3 per cent v/v Flexzone in domestic waste fed to Glendale STP activated sludge. No pH control applied.

Phase (2)

3 per cent v/v Flexzone in domestic waste fed to Elmira STP activated sludge (acclimatized) with feed pH adjusted to approximately 7.0.

Phase (3)

Parallel operation and comparison of Phase (2) tank with another system which was under identical conditions except for no pH control.

Phase (4)

Repeat of Phase (2) with the goal of improving BOD and COD reductions.

Bio-assays performed by Mrs. T. Lambert of the Biology Branch, as outlined in her memorandum of October 20, 1967, relate to the various

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phases of TAS biological treatment as follows:

Phase (1) - Biology #BY 88

Effluent produced mortality at 10% v/v. In this phase of biological treatment, BOD reduction averaged 67% and COD reduction 64%.

It is noted that the unneutralized 3% v/v solution of Flexzone in domestic waste had a pH >12.0.

Phase (2) - Biology #BY 93 and 93A

Mortality produced at 50% v/v in #BY 93 and 32% v/v in #BY 93A.

BOD and COD reductions here were poor at approximately 50%. Neutralization of the raw feed to the activated sludge process probably accounted for the reduced toxicity.

Phase (3) - No samples submitted to Biology Branch

BOD and COD reductions on samples from both the alkaline and neutralized systems were very good at a consistent 85% or more.

Phase (4) - Biology #BY 157

Mortality produced at 5.6% v/v. Although the toxicity of the effluent in this phase was very high, BOD and COD reductions were good at a consistent 90% or more. High toxicity probably due to high BOD and COD in effluent samples. The BOD was about 200 and COD about 220 in these samples, despite reductions of >90%. In the other phases of treatment, BOD and COD were lower in the effluent samples, despite inferior reduction, as the influent BOD and COD's were considerably lower.

The Building 8 sample proved to be easily treatable and showed no toxicity at all.

To summarize briefly, the Flexzone waste is biologically treatable with a little effort such as pH control. The effluents from our systems were always toxic, but at levels which are probably negligible when initial dilution by the receiving stream is considered. Another point worthy of note is that this waste at Elmira will have ten days retention in the holding pond, which will probably reduce BOD, COD, and toxicity to some degree before the waste reaches the sewage plant.

Original by,

J. Smart

APPENDIX VI

Inter-Office Memorandum

Date: April 9, 1968.

To: Central Records

From: Mr. R. A. Abbott, Division of Industrial Wastes.

Re: UNIROYAL (1966) LIMITED, ELMIRA
WASTES TREATABILITY STUDY, FEBRUARY, 1968

Two waste streams were studied in this investigation, namely, Building 8 sump wastewater, including flexzone wastes, and wastes from the general waste sump (MBT and ADAM wastes). These wastes represent approximately 80% of the total contaminated waste flow from the Uniroyal plant.

The treatability studies were carried out in 20 litre model units using sludge from the Elmira sewage treatment plant and raw sewage from the Glendale sewage treatment plant. Dilutions of the two wastes in Glendale sewage were prepared, initially at levels somewhat lower than those prevailing at the Elmira sewage treatment plant. These concentrations were gradually increased and the feed rates on the model units adjusted until loading conditions and retention time corresponded to the Elmira sewage treatment plant. Frequent checks on MLSS and specific oxygen uptake rate were carried out on both units and influent and effluent samples for BOD and COD and fish toxicity analysis were taken when it appeared that specific oxygen uptake rate and effluent quality had stabilized at an optimum level.

The Building 8 sump wastewater proved to be the most readily treatable; the initial acclimatization period was short, about ten days,

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and the treatment efficiency and S.U.R. were consistently high. Treatment efficiencies in terms of BOD and COD removal were 82% and 91% respectively, at the end of the study, when effluent samples were submitted to the Biology Branch for fish toxicity tests.

The general waste sump sample was found to be less readily treatable. The initial acclimatization period was longer (about three weeks) than that for the Building 8 sump wastewater and specific oxygen uptake rate consistently lower. However, once the sludge had been acclimatized to the waste, a moderately acceptable degree of treatment was achieved. Efficiencies in the order of 80% and 60% removal of BOD and COD respectively were obtained towards the end of the study period.

In summary, it appears that both these wastes are amenable to biological treatment under laboratory conditions, with the MBT and ADAM wastes the least amenable of the two. The important differences between laboratory conditions and those prevailing at the Elmira sewage treatment plant are temperature, uniform feed rate and uniform waste characteristics. It remains to be seen whether these conditions can be duplicated at the sewage treatment plant and a corresponding degree of treatment achieved.

Original signed by,

R. A. Abbott

APPENDIX VII

Inter-Office Memorandum

Date: March 15, 1968.

To:

Mr. B. Boyko,

Division of Research.

From:

Mr. R. A. Abbott,

Division of Industrial Wastes.

Re: CYANIDE WASTES FROM MONEX PRODUCTION AT UNIROYAL, ELMIRA

This will confirm our telephone conversation of February 12 on this matter and my subsequent discussions with Mr. Ross Mills of Uniroyal.

The MONEX rubber chemical was produced on February 9, 10 and 11, 1968 and it was reported, that just prior to this, approximately 2,000 gallons of wastewater from a batch manufactured three months previously were pumped from a holding pond to the lagoon system.

The characteristics of the MONEX wastes, as reported by Mr. Ross Mills, are as follows:

Volume	1.4	gallons per pound of product
NaCN	0.085	pounds per pound of product
Organics	0.24	pounds per pound of product
NaCNS	0.48	pounds per pound of product
Na_2SO_4	1.27	pounds per pound of product

The total MONEX production during the most recent run was 11,000 pounds. Consequently, a waste volume of 15,400 gallons containing about 1,000 pounds NaCN and 5,000 pounds NaCNS were discharged to the holding pond, where it will be retained until the next batch is produced and slowly bled to the lagoon system.

Assuming the wastes from the previous batch had similar characteristics, approximately 2,000 gallons containing 6,000 ppm NaCN and

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30,000 ppm NaCNS were pumped to the equalization lagoons. If this was completely mixed with the lagoon contents, the lagoon effluent would contain 6 ppm NaCN. It is not known to what extent three months storage may have reduced the NaCN or NaCNS content of the wastes or whether the low level of the lagoons at the time and the consequent reduced equalization contributed a shock loading to the sewage treatment plant.

It is interesting to compare the frequency of MONEX production with incidences of operating problems at the sewage treatment plant. According to Mr. Ross Mills, MONEX was produced in February, April, May, July, August, October and December of 1966, in February, April, June, September and November of 1967 and, most recently, in February, 1968. These periods approximately coincide with process upsets or poor effluent quality at the sewage treatment plant, with the exception of February, 1966 and April, June and September of 1967.

This, coupled with your analysis of one lagoon effluent sample of 0.8 ppm cyanide, suggests there may be some relationship between MONEX wastes and process upsets at the sewage treatment plant.

A more precise breakdown of dates of MONEX waste disposal and process upsets at the sewage treatment plant may shed more light on this matter and a regular analytical check for cyanide in the Uniroyal plant effluent is also desirable.

In any event, it seems clear that a better pretreatment or disposal procedure for the MONEX waste is required at the Uniroyal plant than the present so called holding and bleed-off procedure.

Original signed by,

R. A. Abbott

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APPENDIX VIII

Inter-Office Memorandum

Date: April 1, 1968.

To: Mr. R. A. Abbott, Division of Industrial Wastes.

From: Mr. D. L. Wells, Biology Branch.

Re: UNIROYAL LIMITED, ELMIRA
BIO-ASSAY RESULTS, FEBRUARY 15 - MARCH 13, 1968

The following samples were received by the Biology Branch for bio-assay evaluation:

Biology Branch Number	Date	Description	Sender
BY 7	Feb. 15	Raw Flexzone Waste	R. Abbott
BY 8	Feb. 15	Treated Flexzone Waste (15% in sewage)	R. Abbott
BY 9	Feb. 19	Treated MBT and ADAM Waste (8% in sewage)	R. Abbott
BY 10	Feb. 19	Raw MBT and ADAM waste	R. Abbott
BY 13	Mar. 13	Treated MBT and ADAM Waste (8% in sewage)	J. Smart

Range tests were performed on all samples. In the procedure, two fish were exposed to two litre volumes of various concentrations of the waste sample. Aged Toronto tap water was used as the diluent in all cases. The test animals used were fathead minnows (Pimephales promelas) which had been acclimatized to laboratory conditions. The tests were carried out at ambient temperatures (about 21°C) and terminated after twenty-four hours. In receipt, Sample BY 7 had a pH of 12 and was, therefore, neutralized prior to the bio-assay evaluations. All other samples had approximately neutral pH.

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Flexzone Waste

The untreated sample of this waste showed zero % mortality at 1.0% v/v dilution, (see Table 1). The treated sample of the waste showed zero % mortality at 100% concentration (equivalent to 15% raw waste). Thus, the % concentration at which mortality in 24 hours stopped occurring increased from 1% to at least 15%. Throughout the period of the test, dissolved oxygen remained at satisfactory levels.

MBT and ADAM Waste

The untreated sample of this waste showed 50% mortality in 24 hours at 0.01% (see Table 2). After treatment, the same sample showed 50% mortality in 24 hours at 1.0% (equivalent to 0.08% raw waste). Thus, the toxicity was reduced, but not as much as the toxicity of the flexzone waste.

On a repeat test of the MBT and ADAM waste, there was no mortality at the 1.0% concentration of treated waste (equivalent to 0.08% raw waste) although one animal was moribund. The results of the two tests would appear to be quite similar and reproducable.

At 100% concentration. treated waste, the dissolved oxygen fell from 4.5 mg/l to 2.5 mg/l during the test period indicating that the sample had a fairly high oxygen demand.

TABLE 1

Results of Bio-assays on Uniroyal Flexzone Wastes

Sample	Concentration % by volume	% Fish Mortality	Dissolved Oxygen (ppm) Hour 0	Dissolved Oxygen (ppm) Hour 24	pH Hour 0	pH Hour 24
BY 7 Flexzone Waste -untreated	50%	100% in 0.5 hrs.	8.0	8.4	-	8.9
	10.0%	100% in 2.0 hrs.	7.9	8.5	-	8.3
	1.0%	0% in 24 hrs.	9.1	6.6	-	7.5
	0.10%	0% in 24 hrs.	9.1	6.6	-	7.2
	0.01%	0% in 24 hrs.	8.5	6.4	7.4	7.3
	0.001%	0% in 24 hrs.	8.5	6.3	7.4	7.3
	0.000	0% in 24 hrs.	8.4	6.3	7.9	7.3
BY 8 Flexzone Waste -treated (15% sewage)	100%	0% in 24 hrs.	7.6	5.1	-	8.0
	10.%	0% in 24 hrs.	11.9	5.5	-	7.6
	1.0%	0% in 24 hrs.	11.5	4.2	-	7.5
	0.1%	0% in 24 hrs.	11.5	5.4	-	7.2
	0.01%	0% in 24 hrs.	11.5	5.9	-	7.2
	0.00%	0% in 24 hrs.	11.7	4.0	-	6.8

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TABLE 2

Results of Bio-assays on Uniroyal MBT and ADAM Wastes

Sample	Concentration % by volume	% Fish Mortality	Dissolved Oxygen (ppm)		pH	
			Hour 0	Hour 24	Hour 0	Hour 24
BY 10 MBT and ADAM Waste - untreated	50.0%	100% in 0.16 hrs.	5.7	7.5	7.35	8.30
	10.0%	100% in 1 hr.	7.4	7.7	7.50	7.45
	1.0%	100% in 5 hrs.	7.9	7.8	7.40	7.10
	0.1%	100% in 5 hrs.	8.2	7.8	7.50	7.00
	0.01%	50% in 24 hrs.	7.7	5.7	7.35	6.65
	0.00%	0% in 24 hrs.	8.1	6.3	7.55	6.45
BY 9 MBT and ADAM Waste - treated (8% sewage)	100.0%	100% in 1 hr.	4.5	2.5	7.40	7.75
	10.%	100% in 2 hrs.	7.1	6.2	7.45	7.95
	1.0%	50% in 24 hrs.	6.9	6.8	7.55	7.85
	0.1%	0% in 24 hrs.	7.4	6.6	7.55	7.85
	0.00%	0% in 24 hrs.	6.2	6.3	7.50	7.70
BY 13 MBT and ADAM Waste - treated (8% sewage)	100	100% in 24 hrs.	6.9	5.2	8.45	8.30
	50	100% in 6 hrs.	8.4	5.8	8.40	8.25
	10.0	100% in 4 hrs.	9.0	6.4	8.00	8.10
	1.0	*0% in 24 hrs.	9.2	5.7	7.90	7.80
	0.10	0% in 24 hrs.	9.3	6.0	7.80	7.80
	0.00	0% in 24 hrs.	9.2	5.7	7.75	7.80

* - One animal moribund

Original signed by,

D. L. Wells