E. I. du Pont de Nemours & Company

P. O. Box 1217
Parkersburg, W. Va. 26101

PLASTICS DEPARTMENT

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TO:	G. F. CURTIN - Wilmington	S. A. SAVAGE - Parkersburg
	W. A. SHEARER - Wilmington	T. N. SHIPLEY - Parkersburg
	DR. J. W. CLAYTON - Haskell Laboratory	W. L. SMITH (2) - Parkersburg
	W. J. BREHM - ESL	File: 8-0

FROM: C. S. COPE - Parkersburg [signature]

BIOASSAY RESULTS FROM THE PHILADELPHIA ACADEMY OF NATURAL SCIENCES

Introduction

Attached is a report describing the results [illegible]-term bioassay tests on aquatic life, as carried out for us on a confidential basis during the past half year by the Philadelphia Academy of Natural Sciences. Two of the twelve materials submitted for testing were taken from the North and West plant outfalls. The remainder were either waste streams from the "Teflon" plant or ingredients used, or considered for use either now or in the past, for "Teflon" manufacture.

Discussion

The first five columns of the attached table describe the samples submitted and identify them with the code numbers under which they were evaluated at the Academy. In the cases of Samples DDW-1[illegible], 11, and 12, the materials were submitted as aqueous solutions of known concentration. The Academy's results for these three samples are expressed in concentrations based on the amounts of solution used. To express the results in terms of the pure compounds, the "biologically safe concentration" (BSC) values reported must be multiplied by 0.20, 0.20, and 0.158, respectively. These factors have been applied where appropriate in Columns 6, 7, and 8 of Table I of this letter, where the BSC values are listed for sunfish, snails, and diatoms on a parts per million basis. The ppm values can be converted to per cent by multiplying by 0.0001. For each material tested, the BSC value for the type of organism to which the material was found most toxic (lowest BSC value) is underlined, though in most cases the toxicities of any one mater[illegible] toward the three types of organism were of a comparable order [illegible]. Since the tests on fish, snails, and diatoms [illegible] in different vessels, this compa[illegible]ility incre[illegible] the data obtained.

In the final column of the table, available data on toxicities toward rats, as measured at Haskell Laboratory and elsewhere, are listed.

The reported toxicities of "Triton" X-100 and "Tergitol" 15-S-9 to aquatic life are high. A saturated aqueous solution of iodine and iodine-containing compounds from a Telomer "A" reactor residue was about one-tenth as toxic as the above surfactants. The ammonium salt of chlorendic acid (the form in which we would plan to dispose of chlorendic acid) was as toxic to fish as C-8 APFC and C-9 AFC, though the latter compounds are about twice as toxic to snails as to fish. Possible conversion of the ammonium salt to the acid form in the river would lead to considerably increased toxicity, however. As earlier found for rats, AHT was considerably more toxic than were C-8 and C-9. The effluent from the HCl neutralizer in the monomer refining system was essentially non-toxic, as were grab samples taken from both the North and West plant outfalls.

Not too surprisingly, the correlation, over the full spectrum of materials submitted, of relative toxicities toward aquatic life and toward rats is poor. Although no mechanisms are suggested in the report as to the modes of toxi[illegible] the various materials tested, we feel the toxicities toward aquatic life are much more closely related to the surface activities (as measured at low concentration levels) of the test materials than is true for ingestion of these materials by animals. Available data on surface tension versus concentration for the test materials are given in Table II, and it can be seen that the compounds most highly toxic to aquatic life are also the most surface active. Within the class of highly fluorinated surfactants (C-8 APFC, C-9 AFC, FC-95, and AHT), toxicities toward both aquatic life and rats correlate roughly with surface activity. It seems reasonable to conjecture, in the case of fish, that a substantial lowering of the surface tension of the aquarium water might well affect the efficiency with which gills are able to transfer dissolved oxygen from the water for use by the fish.

Concerning the reported high toxicities of "Triton" X-100 and "Tergitol" 15-S-9 to aquatic life, we feel the following items of evidence to the contrary should be cited:

Rohm and Haas Company recently made available to Du Pont a document, written by Dr. K. A. Booman, a chemist in their Research Division. This report, entitled "The Biodegradability of Nonionic Surfactants, a Comparison of Test Methods and Products," was cleared by R & H's Legal Department before being released to us. In it, the following statements appear:

"We are natural[illegible] the possible effect of surfac[illegible] on aquatic [illegible], clams, oys[illegible]. The literature on this subject is quite limited. Nevertheless, the literature that exists suggests that alkylphenol ethoxylates and alkyl aryl sulfonates are comparable in toxicity to aquatic life; comparable and acceptable."

Since "Triton" X-100 is a typical alkylphenol ethoxylate, the above wording "... and acceptable" would appear to be clearly at odds with the findings of the Philadelphia Academy. There is some support ˆ r the Rohm and Haas statement in that we have in the past observed no marked instances of fish being killed when "Triton"-containing liquid was discharged directly to the Ohio River (no longer practiced). Also, Dr. H. J. Schneider of Rohm and Haas' Philadelphia Sales Office, in a visit to Washington Works several months ago, indicated that no known adverse effects on aquatic life have been encountered in the 25 years the "Triton" product line has been on the market (Letter, J. G. Ostroot to T. N. Shipley, 6/15/66).

We feel that consideration should be given to releasing the Philadelphia Academy's results (for "Triton" only) to Rohm and Haas for resolution of this important problem, after consultation with our Legal Department as to the liabilities, if any, we would be assuming in doing so.

It should be noted that the possible effects of chronic exposure cannot be estimated from these short-term tests, although in the case of the diatoms the organisms passed through several generations during the course of the bioassays. However, we see no urgency at this time in embarking on a program of measuring chronic effects, evaluation of which would be more expensive and fairly time-consuming.

Table III lists analyses of Ohio River water at Parkersburg which were supplied to the Academy for their use in preparing a synthetic equivalent for the bioassay testing.

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Attachments

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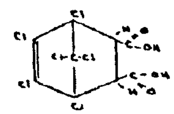
HASKELL LABORATORY

TABLE I

BIOASSAY RESULTS FROM PHILADELPHIA ACADEMY OF NATURAL SCIENCES

Code Number	Material	Structural Formula	Form	Solubility In Water	Biologically Safe Concentration, ppm** Sunfish	Snails	Diatoms	Toxicity Toward Rats***
DDW-1	Ammonium perfluorooctanoate ("C-8 APFC")	$CF_3(CF_2)_6COONH_4$ (containing some branched isomers)	Powder	High	465	246	720*	ALD = 670 mg/kg
DDW-2	Ammonium ω-hydro hexadecafluorononanoate ("C-9 APFC")	$HF_2C(CF_2)_7COONH_4$	Powder	High	465	224	465*	ALD = 1500 mg/kg
DDW-3	Chlorendic Acid		Powder	Low (0.35%)	62	100	186	ALD = 2250 mg/kg
DDW-4	Ammonium Chlorendate	(Di) ammonium salt of above	Powder	Moderate (10.35%)	465	240	2400*	Presumably less toxic than chlorendic acid
DDW-5	Potassium salt of C-8 perfluorosulfonic acid	$CF_3(CF_2)_7SO_3K$ (containing some branched isomers)	Powder	Low (0.2%)	67	77	96	ALD = 500 mg/kg
DDW-6	Telomer "A" Reactor Residue (Sat'd Aq Soln.)	(Various compounds, including free iodine and compounds of antimony and iodine)	Liquid	—	140	110	285	Not tested
DDW-7	Effluent from HCl Neutralizer, TFE Plant (pH = 8.0)	$CaCl_2$ + low concentrations of fluorocarbon compounds	Aqueous liquid (small amount of sediment present)	—	120,000	60,000	172,000	-----------
DDW-8	Sample of North plant outfall, collected over 24-hour period (pH = 6.6)	(Various compounds)	Aqueous liquid	—	300,000	300,000	~300,000	-----------
DDW-9	Similar to above, but from West plant outfall (pH = 7.0)	(Various compounds)	Aqueous liquid	—	300,000	300,000	187,000	-----------
DDW-10	"Triton" X-100 (Rohm & Haas) (Condensation product of t-octylphenol and ethylene oxide)	$C_8H_{17}\phi(OCH_2CH_2)_xOH$ (x = 9-10)	Aqueous solution (20.0 gms Triton per 100 ml)	—	16	12	28	LD-50 = 1900 mg/kg
DDW-11	"Tergitol" 15-S-9 (Union Carbide) (Condensation product of 15-C atom alkyl secondary alcohol and ethylene oxide)	$C_{15}H_{31}(OCH_2CH_2)_xOH$ (x = 9)	Aqueous solution (20.0 gms "Tergitol" per 100 ml)	—	11	7	3	Presumably comparable to "Triton" X-100
DDW-12	Ammonium-3,6-dioxa-4,5-bis (trifluoromethyl) undecafluorononanoate ("ANT")	$CF_3CF_2CF_2OCFCF_2OCFCOONH_4$ with CF_3 groups on the two CF	Aqueous solution, sp gr = 1.048 (15.2 gms ANT per 100 ml)	—	120	193	24*	ALD = 60 mg/kg

* "Clumping" of diatoms observed during tests of reduction in growth.
** See text of letter for details as to basis on which these values are listed.
*** Rat toxicity data were taken from Haskell Laboratory reports, except for DDW-10, taken from Rohm and Haas' Trade Bulletin, "Triton Surface-Active Agents -- The Nonionic Octylphenoxyethanol (OPE) Series", 57-59, 6/59.

TABLE II

CONCENTRATION IN WATER, WEIGHT %/SURFACE TENSION, DYNES/CM AT 25°C

Code Number		Order of Decreasing Activity (at low concentrations)
DDW-1	0.10/53.5 0.30/40.5 0.70/29.5 1.1/23.5	3
DDW-2	0.30/50.0 0.65/40.0 1.0/33.0 1.4/27.0	5
DDW-3	Saturated Solution/42.0 (~0.35%)	4
DDW-4	Virtually non-surface-active	6
DDW-5	0.001/62.0 0.01/53.0 0.05/41.0 0/10/36.0 0.22/33.0	2
DDW-10	0.001/46.5 0.0026/40.0 0.0055/35.0 0.01/30.2 0.1/30.2	1
DDW-11	Believed similar to DDW-10 0.10/29.4	(1)
DDW-12	0.02/50.5 0.04/46.0 0.10/38.0 0.40/21.5	2

Note: In all cases, there is only a small further decrease in surface tension at concentrations highe? than the final value listed for each material.

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TABLE III

OHIO RIVER WATER (AT PARKERSBURG)-ANALYSES BY BETZ LABORATORIES

All concentrations given are in parts per million by weight.

Date	9/7/60	7/23/65	Typical Range, Plant Analyses
Hardness (as $CaCO_3$)	212	204	150-300
Ca (as $CaCO_3$)	150	148	---
Mg (as $CaCO_3$)	62	56	---
Alk (as $CaCO_3$)	10	40	---
SO_4	177	176	90-300
Cl	68	82	30-150
SiO_2	1.8	0.9	---
pH	5.6	6.8	6.0-8.0
Conductivity, micromhos	---	600	---
Fe	0.15	3.3	0.05-1.2
NO_3 (as N)	1.3	1.0	---
Mn	0	0.7	0.10-2.0
Color (Hazen Scale)	---	30	---
Total Dissolved Solids	346	534	---
Loss on Ignition	---	206	---
Dissolved Oxygen	---	---	Saturated throughout year at prevailing water temperatures.

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