environment

Phthalate Esters Undergo Ready Biodegradation

THAT'S THE GOOD NEWS! SINCE THE PHTHALATE ESTERS DO NOT LEAD TO "BIOACCUMULATION," AS CHLORINATED HYDROCARBONS DO, USERS NEED BE CONCERNED ONLY WITH "AMBIENT" ENVIRONMENTAL LEVELS

Although the words "biodegradability" and "biodegradable" have become household terms, their significance is little understood. These terms first reached the public largely as a result of the development and subsequent extensive consumer use of synthetic surfactants. Foam problems stemming from the discharge of synthetic surfactants into our rivers and streams graphically illustrated the need for biodegradable waste products. Researchers ultimately met the foam problem by switching surfactants, replacing a branched alkylbenzene sulfonate with the more readily degradable linear alkylbenzene sulfonate (1).

A subsequent matter of public concern was triggered by the startling revelation of the persistent nature of DDT and other chlorinated hydrocarbons. The resistance of these chemicals to biodegradation and their potential danger to the environment came to light only after years of extensive use.

Now, another class of industrial chemicals has come under suspicion—the phthalate ester plasticizers (2 and 3). Again, society was confronted by the agonizing question: Could this class of compounds be numbered among those, which because of their natural persistence, menace the environment? We decided to find out by determining their biodegradability—or rate of biodegradation; which can best be defined as the "conversion of chemicals which are potential environmental contaminants to innocuous substances via the biological action of living organisms." As suggested by the term biodegradability, many levels or degrees of biological action can be identified within the framework of this general definition. The initial level or action is termed *primary biodegradation*, i.e., "the minimum alteration of the chemical structure of the material in question to an extent that the characteristic properties of the original material are no longer evident"; the final level is termed *ultimate biodegradation*, i.e., "complete conversion of the material in question to carbon dioxide, water, inorganic salts, and products normally associated with the natural processes of living organisms."

In our environment by far the most important organisms capable of degrading and recycling organic chemicals are bacteria. Bacteria are highly adaptive and capable of utilizing a virtually endless variety of organic compounds both as food and energy sources. Thus, the most logical way to measure biodegradation is to expose test compounds to bacteria under environmentally related conditions and to monitor their fate monitoring the results by suitable analytical methods.

The tests chosen to compare the biodegradability of the phthalate ester plasticizers and intermediates to synthetic organic chemicals of known environmental history are the Soap and Detergent Association's Semi-Continuous Activated Sludge (SCAS) biodegradation test (4 and 5) and the River Die Away (RDA) test (6). The activated sludge test simulates what is probably the most widely used waste water treatment process today and the one that has been selected for many future large waste water treatment installations in the United States. The test was chosen because the fundamental biochemical reactions by which organic chemicals are degraded are the same as those in other aerobic biological treatment units, and because it

Figure 1 (left). Chamber for performing Semi-Continuous Activated Sludge (SCAS) test. Device has provisions for aerating, stirring, and siphoning samples of supernatant.

Figure 2 (right). Mechanical cycle. The synthetic sewage added at the beginning of each cycle consists of 300 milligrams of glucose, 200 milligrams of nutrient broth, and 130 milligrams of dibasic potassium phosphate.

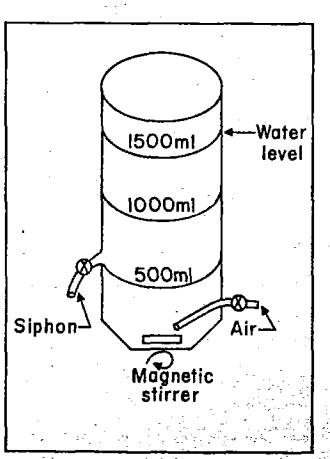

Figure 1

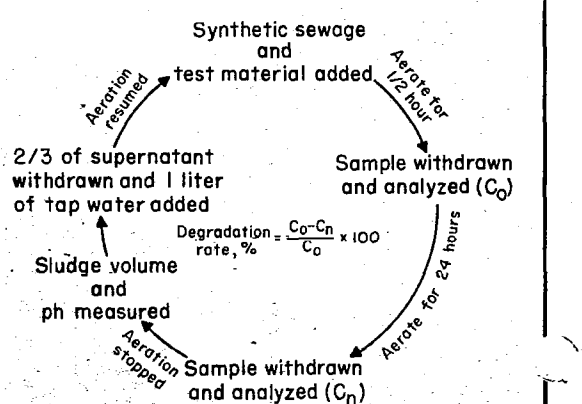

Figure 2

DSW 587815

STLCOPCB4093151

can be readily carried out in the laboratory. The RDA test was used because it more closely represents a natural environmental situation.

SCAS Degradation Rates

Sludge from a domestic sewage treatment plant is the source of microorganisms for the test. The sludge, a specified amount of material being evaluated, and a synthetic sewage mixture are combined in a specially designed aeration chamber (*Fig. 1*), which is a large glass cylinder (85 millimeters in diameter by 60 centimeters high) with provisions for aerating, stirring, siphoning, and removing supernatant (material floating on the surface). The mixed liquor, i.e., the bacterial sludge, water, etc., obtained from a local sewage treatment plant was initially adjusted to a suspended solids concentration of 2500 milligrams per liter by dilution with tap water; and subsequently 1500-milliliter portions of this mixture were used to charge each of the several aeration chambers used in the test. The chambers were operated in a cyclic fashion, as shown in *Fig. 2*, with each cycle initiated by the addition of synthetic sewage and several milligrams of the phthalate ester or intermediate being evaluated. Since phthalate esters are quite water insoluble, they were added by way of syringe injection of a concentrated ethanol solution to obtain a homogenous dispersion. Aliquots or equal portions of the mixed liquor were withdrawn from the chamber at the times indicated in *Fig. 2* and analyzed. The cycle was repeated until steady-state and consistent degradation rates were observed.

A typical example of the data obtained is shown in *Fig. 3*. Here we have plotted the day-by-day behavior of a chamber fed with monobutyl phthalate. The settled sludge volume and pH of each chamber were also monitored daily for satisfactory operation. Once a week the suspended solids concentration was checked gravimetrically and readjusted to the initial concentration level of 2500 milligrams per liter. The percent degradation was calculated, as shown in center of *Fig. 2*, from the amount of test material found in the samples analyzed during each cycle. The *Table* gives the chemical name, addition rate, percent primary degradation rate (±95 percent confidence limits), and method of analysis for each compound studied. Linear alkybenzene

Primary bacterial degradation Semi-Continuous Activated Sludge test.

Compound tested	Addition rate, mg/24 hr	Degradation rate, ±95% C.L.[a]	Method of analysis
1-phenyl dodecane p-sulfonate sodium salt (linear alkylbenzene sulfonate)	20	99+	Calorimetric methylene blue procedure
Phthalic acid	50	99+	
	100	99+	UV/Direct[b]
	200	99+	
Monobutyl phthalate	100	99+	UV/Direct[b]
Butylphthalylbutyl glycolate	5	99+	
	20	99+	
	100	99+	Extraction/GC[c]
	200	99+	
Butylbenzyl phthalate	5	93 ±6	Extraction/GC[c]
	200	99+	
Di(2-ethylhexyl) phthalate	5	70 ±11	Extraction/GC[c]
	5	78 ±3	
Di(heptyl, nonyl, undecyl) phthalate	5	52 ±10	Extraction/GC[c]
	10	48 ±8	Extraction/UV[b]
	20	54 ±7	Extraction/GC[c]
p,p'-DDT [1, 1, 1-trichloro-2, 2 bis(p-chlorophenyl)] ethane	1	−7 ±16	Extraction/GC[c]

[a] C.L.: confidence limit.
[b] UV: ultraviolet spectrophotometry.
[c] GC: gas chromatography.

The Soap and Detergent Association's Semi-Continuous Activated Sludge (SCAS) test and the River Die Away (RDA) test were used to ascertain the primary and ultimate biodegradability of representative phthalate ester plasticizers and pertinent intermediates. Well-documented test results demonstrate conclusively that these products can be regarded as a class of industrial chemicals that are readily degraded by natural biological processes as compared with other industrial products. Water for the RDA test was easily the real thing; it came from the Mississippi River at St. Louis.

Victor W. Saeger and
E. Scott Tucker III,
Monsanto Company,
St. Louis, Missouri

DSW 587816

STLCOPCB4093152

sulfonate, which has a degradation rate of 99+ percent at an addition rate of 20 milligrams per cycle, served as a standard. Phthalic acid, monobutyl phthalate, butylphthalylbutyl glycolate, and butylbenzyl phthalate all underwent complete degradation during each cycle, in some cases at addition rates as high as 100 to 200 milligrams per cycle.

A primary biodegradation rate of 70 to 78 percent was observed for di(2-ethylhexyl) phthalate. Tests of this ester were run twice using sludge obtained from two different sources to demonstrate that the primary degradation rates being observed were independent of the sludge source. To determine whether the degradation rates being measured were also independent of the method of analysis as well as of the addition rate, a plasticizer product containing all combinations of heptyl, nonyl, and undecyl phthalate esters was tested at addition rates of 5, 10, and 20 milligrams per cycle and monitored by both gas chromatography and ultraviolet spectrophotometry. Measured primary degradation rates of 52, 48, and 54 percent, respectively, confirmed the independence of the rate of degradation in the range studied.

To focus more sharply on the difference between degradable and nondegradable synthetic chemicals, tests were concurrently carried out on p, p'-DDT, a known persistent environmental contaminant. A primary biodegradation rate of -7 ± 16 percent was observed at the relatively low addition rate of 1 milligram per cycle. A negative mean degradation rate occurs when the biodegradability of a compound is so low that the inherent uncontrollable experimental variability of the test greatly exceeds the degradation rate.

Ultimate Bacterial Degradation

Once establishing the fact that an organic compound readily undergoes primary bacterial degradation, the ultimate fate of intermediate degradation products becomes the next matter of concern. Anticipated initial intermediate degradation products of the phthalate esters might be either water-soluble aromatic half-esters or phthalic acid, or both. To determine whether water-soluble aromatic intermediates were being produced, experiments were performed with butylphthalylbutyl glycolate, butylbenzyl phthalate, and di-(2-ethylhexyl) phthalate, whereby the filtered aqueous phase was monitored by ultraviolet spectrophotometry for water-soluble aromatics while the mixed liquor was simultaneously monitored for the parent ester. The results obtained for butylphthalylbutyl glycolate ester are shown in *Fig. 4*. The concentration in parts per million of the parent ester and the aromatic water-soluble intermediates (calculated as phthalic acid) is plotted against time. Butylglycolylbutyl phthalate is seen to be quickly converted to water-soluble aromatic intermediates, which then rapidly undergo enzymatic ring cleavage to smaller nonaromatic molecules.

The water-soluble aromatic intermediates shown on the plot were subsequently identified by isolation and comparison with authentic samples of intermediates by derivative gas chromatography. Equivalent results obtained for butylbenzyl phthalate established the fact that these phthalate esters readily undergo ultimate as well as primary biodegradation. With di(2-ethylhexyl) phthalate, no water-soluble aromatic intermediates were detected, an indication that with this ester the intermediates are more rapidly degraded than the parent ester. The actual metabolic pathway by which phthalic acid undergoes ring cleavage was studied by Ribbons and Evans (7) and is shown in *Fig. 5*.

Figure 3. Primary bacterial degradation by Semi-Continuous Activated Sludge test. Test chamber was fed with monobutyl phthalate at an addition rate of 100 milligrams per 24 hours. **Figure 4.** Ultimate bacterial degradation by Semi-Continuous Activated Sludge test. Test chamber was fed with butylphthalatebutyl glycolate ester in concentrations of parts per million. Butylglycolylbutyl phthalate converts to water-soluble aromatic intermediates, which rapidly undergo enzymatic ring cleavage to smaller monaromatic molecules. **Figure 5.** Oxidative metabolism of phthalic acid by soil pseudonomads—the manner in which phthalic acid undergoes ring cleavage.

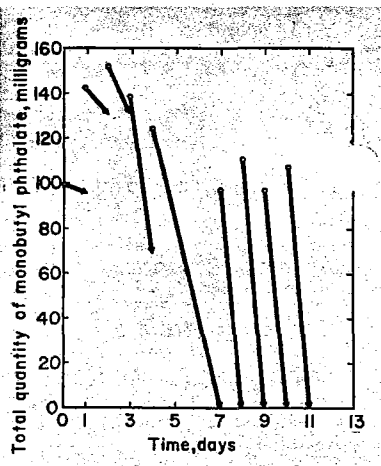

Figure 3

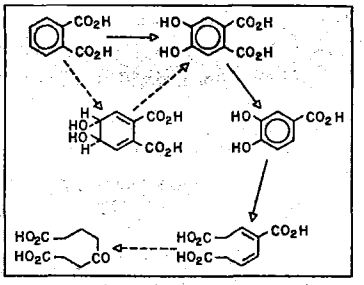

Figure 5

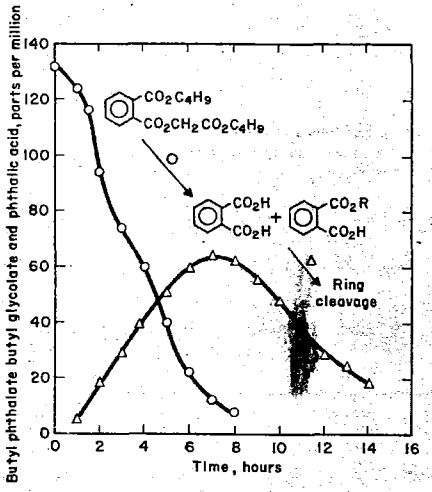

Figure 4

Figure 6. Primary bacterial degradation by River Die Away Test over an approximate 18-day period. Both Butylglycolylbutyl phthalate and butybenyl phthalate undergo degradation more rapidly than the linear alkylbenzene sulfonate reference standard. This is also true for phthalic acid, but at a less-rapid rate. **Figure 7.** Primary bacterial degradation by River Die Away

RDA Bacterial Degradation Rates

At this point, one further question can be asked: Do phthalate esters undergo biodegradation at reasonable rates in real life, such as in a river or stream, where the number of micro-organisms are orders of magnitude lower and the amount of available nutrients are limited? The answer to that question is found in the RDA test, which is very simply performed, in that the basic requirements are a source of river water and a number of clean screw-cap, large-mouth bottles.

Once the river water is obtained, the bulk of the sediment is allowed to settle out and 200-millimeter portions of the supernatant river water are placed in a requisite number of 16-ounce screw-cap bottles. Test compounds are then added to the river water and the bottles loosely

DSW 587817

STLCOPCB4093153

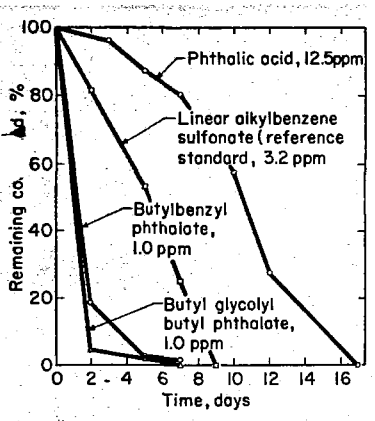

Figure 6

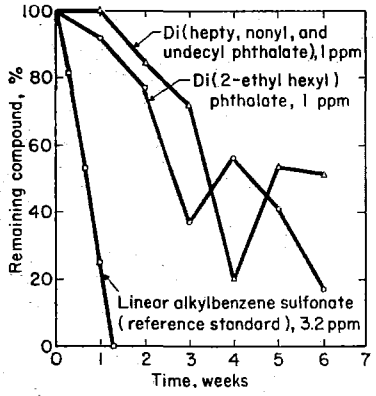

Figure 7

Test over an approximate 6-week period. Esters of di(2-ethylhexyl) phthalate and di(heptyl, nonyl, and undecyl) phthalate undergo reasonably rapid primary biodegradation, but at a slower rate than the reference standard.

sealed. At various times the total contents of a bottle are sacrificed and the amount of test compound undegraded is determined by the appropriate method. Sterile distilled water controls are run concurrently to ensure that the disappearance of the test compound is due to biodegradation and not to chemical or physical reaction.

The results of the RDA degradation studies are shown graphically in *Figs. 6* and 7. In each figure, the percent of test compound remaining is plotted against exposure time. The die away curve for the linear alkylbenzene sulfonate reference standard is included on each figure. The water used in these tests was obtained from the Mississippi River at St. Louis, Mo.

Figure 6 shows how two of the plasticizers studied—butylglycolylbutyl phthalate and butylbenzyl phthalate—underwent primary degradation more rapidly than the alkylbenzene sulfonate standard. Curves for di(2-ethylhexyl) phthalate and the mixed di(heptyl, nonyl, and undecyl) phthalate ester (*Fig.* 7) show that both of these esters also underwent reasonably rapid primary biodegradation, but as anticipated from the SCAS data, at a slower rate than the reference standard.

Conclusions

The importance of utilizing industrial products which readily undergo degradation lies in the fact that as long as their rate of release does not greatly exceed the rate at which they are degraded we need only concern ourselves with the impact of the ambient environmental level and not so much with accumulation as in the case of persistent chlorinated hydrocarbons such as DDT.

Our tests clearly demonstrate that the phthalate ester plasticizers and intermediates are rapidly degraded by readily available bacteria in our environment. For this reason, we feel that they should not be classified as persistent materials but rather as a class of industrial chemicals which are easily recycled by natural biological processes.

References

1. R. D. Swisher, "Surfactant Science Series, Surfactant Biodegradation, Vol. 2, Marcel Dekker, Inc., N.Y. (1970).
2. D. L. Stalling, F. L. Mayer, and J. L. Johnson, *Nature*, 238, 411 (1972).
3. *Environmental Health Perspectives*, U.S. Dept. of HEW, Public Health Service, National Institute of Health, Experimental Issue No. 3, Jan. 1973, DHEW Publication No. (N1H) 73-218.
4. Soap & Detergent Association, Biodegradation Subcommittee, Procedure and Standards for Determination of Biodegradability of ABS & LAS, *Amer. Oil Chem. Soc.*, 42, 986 (1965).
5. Soap & Detergent Association, The Status of Biodegradability Testing of Nonionic Surfactants, *Amer. Oil Chem. Soc.*, 46, 432 (1969).
6. P. J. Weaver and F. J. Coughlin, *Amer. Oil Chem. Soc.*, 41, 738 (1964).
7. D. W Ribbons and W. C. Evans, *Biochem. J.*, 76, 310 (1960). □

For free reprint of this article see page 258.

panoRAMa . . .

per Mr. Webster, is "an unobstructed view over a wide area." Not to brag, but somehow it reminds us of us.

As starters, Doc and Al Steinman are still holding forth at the old stand even as we pass through RAM's silver anniversary year. Both are plenty generous sharing experience with those of us more recent. Consequently, we have quite a collection of FRP lore.

It doesn't all involve matters historic, either. We pick up new things every day. Example: who'd ever guess a simple inert like walnut shell to be the basis of a tragedy in filled polyester moldings? (Exothermic heat made its oil content exude, causing pre-applied primer coating to spring loose after demolding the parts).

RAM people who deal with the public are full of such heady information. Plenty of the "tricks of the trade" don't necessarily involve RAM products directly, but that doesn't prevent us from sharing the knowledge.

The upshot: down-to-earth solutions often come easily when matters turn frazzled at your end. We answer our mail the day we get it. If the problem warrants spending a phone call, you're guaranteed an attentive ear.

Ten years back, some earlier RAM ad copy boasted, "Our staff loves problems others have failed to solve . . . send us one. You'll be happy . . . or *we'll* have a new staff (or more cautious advertising!)."

RAM hasn't backed away yet.

GEL COATS • RELEASE AGENTS
PIGMENTS • MOLD PREP
PRIMERS • CATALYSTS
COATINGS • REINFORCEMENTS

RAM chemicals

A DIVISION OF Whittaker CORPORATION

210 EAST ALONDRA BOULEVARD
GARDENA, CALIFORNIA 90247
TELEPHONE: (213) 324-6116 (321-9710

DSW 587818

STLCOPCB4093154

How to build a moldmaking reputation in 60 seconds.

D·M·E STANDARDIZATION CAN DO IT FOR YOU

Simply call your D-M-E branch. Let them supply the finished, precision mold bases, components, cavity insert rounds and blocks and special machining services you need, while your crew concentrates on cutting cavities. Your cavity output goes up. Your time-per-completed-assembly goes down. And you build a reputation for both precision work *and* fast delivery. Your local D-M-E branch can supply *everything* you need, quickly, at less cost than you can make it for. They have in stock mold bases ranging in size from 3½ x 3¾ to 23¾ x 35½, for immediate shipment.

See the Yellow Pages under "Molds" for your nearest D-M-E branch. They're located throughout the U. S., and in Canada, Mexico and Europe.

If you're interested in injection or compression molding, you should know D-M-E.

D-M-E where quality is assured.



D·M·E CORPORATION

DME Subsidiary of VSI Corporation VSI

STLCOPCB4093155