

Responsible Effluent Disposal

Tests verified the spent processing solution effluents did not have toxic effects on municipal treatment plant bacteria.

..... by Peter S. Strliko

Under the federal Clean Water Act, the Environmental Protection Agency (EPA) established effluent guidelines for the metal finishing and electroplating industries covering discharges to Publicly Owned Treatment Works (POTWs) and to surface waters. These regulations materially influence the way industry must function, and impact the bottom-line profitability of manufacturing operations.

The local municipalities, districts, or counties generally administer these regulatory programs under delegation through the states. These local agencies establish the prevailing sewer use codes industry is required to meet. According to federal law, all POTWs accepting industrial discharges from these industries must incorporate the federal effluent guidelines into local sewer use permits or adopt more stringent limits.

Manufacturers who discharge their effluent to surface waters (streams, rivers, lakes) are considered direct dischargers and must operate under a National Pollutant Discharge Elimination System (NPDES) permit or similar state permit (SPDES). Direct discharge effluent limits are generally an order of magnitude more stringent than those required by the POTW.

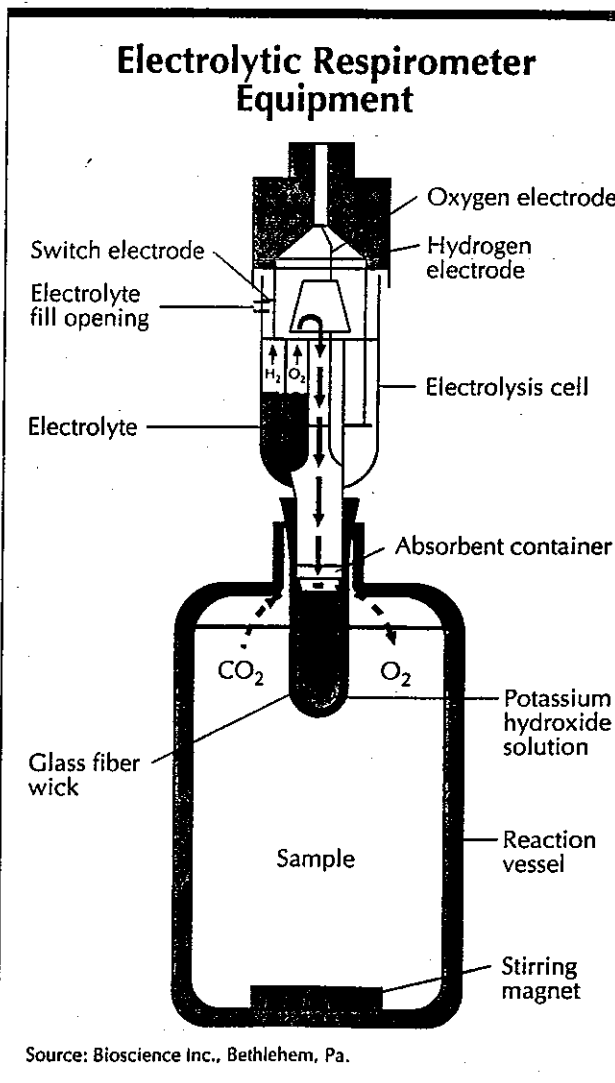
The effluent guidelines are directed toward a set of Priority Pollutants comprising toxic metals such as lead, nickel and copper; toxic organics including a listing of 109 organic substances known as total toxic organics (TTO); and cyanide.

Another group of wastewater characteristics is often referred to as conventional pollutants. This incorporates a variety of factors principally indicating the aggregate characteristics of the effluent, such as pH, total suspended solids (TSS) and organic strength.

PWB wastewater characteristics

Printed wiring board (PWB) manufacturers are concerned about copper or lead concentrations in their plant wastewater effluent compared with permissible daily limits or more stringent multiple day averages. In addition to metals, the second most important components in plant effluents are organic materials, principally from the variety of cleaners, de-

fluxing agents, surfactants, defoamers and photopolymer processing solutions. In fact, the photopolymer processing solutions consisting of spent developers and strippers often comprise the largest single contributor to organic strength of the PWB fabrication process effluent. When water-soluble organic cosolvents are incorporated, as is common in proprietary strippers and semi-aqueous dry film resist processing, the percent of total organic strength at-



● Figure 1. Electrolytic respirometry permits oxygen uptake by the bacteria to be continuously and accurately monitored electronically.

tributable to these photopolymer processing solutions can reach or even exceed 90 percent of the plant's total output.

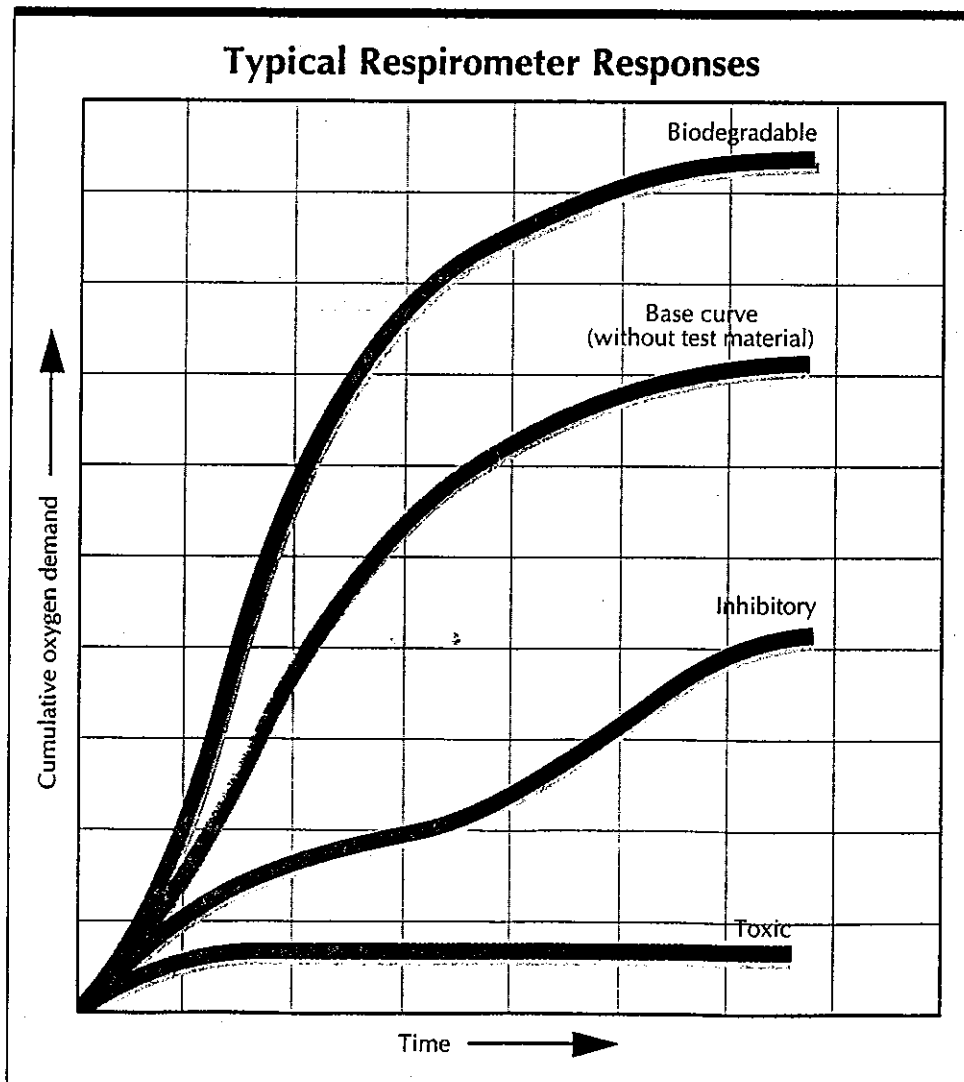
Some understanding of the processes and how the spent photopolymer processing solutions interact should be of some importance both to PWB manufacturers discharging these effluents, as well as to the POTW regulatory and operating personnel who accept responsibility for treating them.

In a typical PWB fabrication, spent photopolymer solutions may comprise only 1 to 2 percent of the volume of plant effluent. In mass lamination facilities doing only print and etch panels or where significant water conservation and reuse is practiced, this may increase to more than 5 percent. These spent solutions are generally metered into the total plant effluent at final pH adjust, immediately prior to entering the sewer collection system. This comingling of photopolymer effluents with other effluent streams, such as the discharge from the heavy metal waste treatment facility or other non- or low-metal bearing streams is permissible under federal law since they all result from the total integral process of PWB manufacture.

Spent developers are quite low in metal content, usually well below prevailing sewer use codes, so these can often be introduced to the final plant discharge as described above. Spent strippers present a significantly different situation. The water soluble active components required to make the stripper chemistry effective, react with the metals (copper, lead and tin) on the PWB surface. Therefore, spent stripping solutions may contain enough heavy metals to require special waste treatment, off-site disposal, or at a minimum, a thorough understanding of all factors involved in on-site disposal or treatment.

Solvent vs. aqueous

The introduction of semi-aqueous and aqueous processing photopolymer films in the early 1970s brought a new series of challenges. As the science has advanced and the regulatory picture has unfolded, chlorinated solvents have been largely replaced with water-based processing chemistries. The conversion to aqueous-based processing chemistries is now 90 to 95 percent complete in North America, South America and Asia Pacific, with Europe and Japan



● Figure 2. The cumulative oxygen demand curves demonstrate the biodegradability and toxicity of test solutions.

There are practical limits to organic strength at which bacteria effectively biodegrade organic substances.

fast approaching that level.

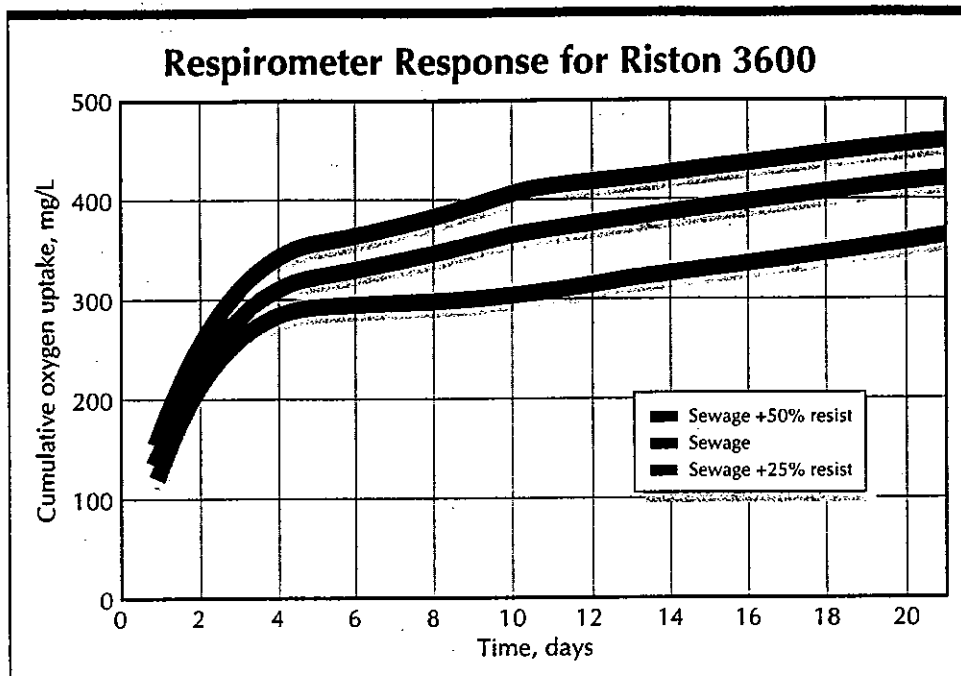
By way of comparisons, sludges drained from the still for the solvent process were quite concentrated, generally reaching 25 percent by weight or more of photopolymer film. These were drummed for off-site recovery and destruction. For solvent assisted or semi-aqueous processing, the spent solutions rarely exceed 2 or 3 percent by weight; in fully aqueous processing chemistry, the concentration of dissolved photopolymer is generally less than 1 percent; and from a feed-and-bleed operated developer, can drop

to as low as 0.3 percent by weight. For the range of typical PWB fabricators, the volumes of spent aqueous and semi-aqueous processing developers and strippers are sufficiently large that alternate paths of disposal had to be considered. Clearly, disposal to the municipal sewer system is the preferred alternative.

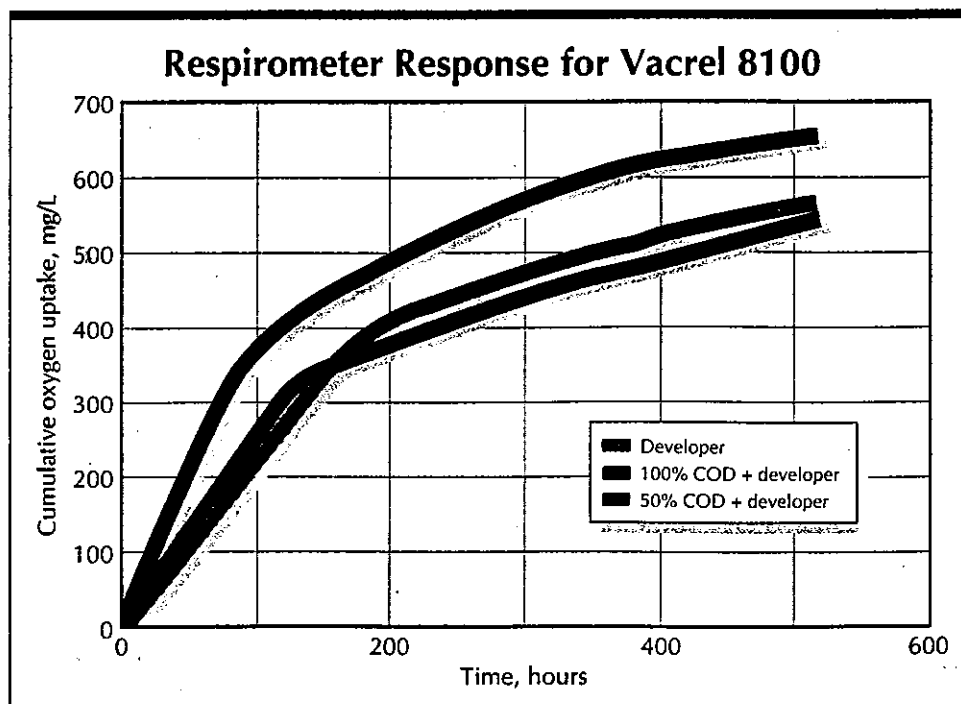
Biological wastewater degradation

Biodegradation is a process whereby bacteria, normally found in streams, rivers, and sewer biological wastewater treatment systems, degrade many organic

● Figure 3. The test solution was comprised of equal amounts of developer and stripper at organic strengths equivalent to 20 and 33 percent of the total organic strength arriving at the POTW. Even at these high concentrations, the oxygen uptake curves verify that the spent solutions do not exert toxic or inhibitory effects on the bacteria.



● Figure 4. In this test, dosing of spent solder mask developer solutions is based on its COD. The curves confirm that the bacteria continue to function optimally at the higher dosing.



substances, including human waste, household waste, and many industrial effluents, generally to carbon dioxide and water. This oxidative process, called aerobic degradation, requires an oxygen source, usually supplied by air, which is absorbed into the wastewater for the bacteria to utilize.

The amount of oxygen uptake gives a measure of the organic strength of an effluent. Oxygen uptake is usually measured over a five-day period and indicated in milligrams of oxygen uptake per liter of solution (mg/L). The test is referred to as BOD₅. Occasionally the tests are run over longer periods of time where information on more extended biodegradation can be obtained, for example, BOD₂₀.

There are practical limits to organic strength at which bacteria can effectively and efficiently biodegrade organic substances. When the organic strength becomes too high, efficiency of the bacteria will be reduced. If the organic strength becomes extremely high, it will kill the bacteria. When laboratory BOD₅ tests are conducted on high organic strength effluents, it is common to perform a series of BOD₅ tests using different dilutions with water. The resulting oxygen uptake values are then extrapolated back by the dilution factor to obtain the actual BOD₅ for the test solution.

When a BOD₅ series of this type is evaluated, it is common to observe a diminished oxygen uptake at the high end of organic strengths at which the bacteria are tested for the aforementioned reason. Therefore, the value of BOD₅ actually reported will be the maximum oxygen uptake observed in the test series. When a test solution is brought to a laboratory for testing, the bacteria used may be from a stream or sewer system. When using this type of bacteria, which is not specifically prepared or acclimated, the BOD₅ is referred to as unacclimated BOD₅.

Bacteria are living colonies or populations of differing bacterial types. Some strains of bacteria can more efficiently biodegrade a given waste than others. While we tend to think of bacteria in terms of their degrading action on organic substances, it is important to understand that these organic substances are actually the food supply that sustains these bacteria. The populations of bacteria in a colony are dynamic and will undergo changes in response to the available food supply. If a new test material is introduced, the strains of bacteria that can best assimilate it will proliferate. These changes to the bacteria population do not occur immediately, but often take several weeks before the concentration of these more efficient types of bacteria reach a population density that is appropriate for the abundance of the food supply. The population then stabilizes.

To maintain bacteria in the laboratory, it is necessary to provide them with a source of oxygen and a food supply. Small amounts of a test solution (for example, photopolymer developer and stripper that has been carefully neutralized to avoid generating any precipitate) are incorporated into the food supply at progressively larger amounts, often up to 30 percent of the total organic strength. The progress of the changes to the bacterial population, as is manifested in an enhanced ability to biodegrade this test solution,

can be monitored. This is done by periodically measuring BOD₅ of the test solution using these same bacteria. Prior to the introduction of the test solution to the bacteria nutrient supply, a BOD₅ test is run with that bacteria to determine the unacclimated value. Additional weekly BOD₅ tests are run with the same test solution and using the same bacteria but which is now undergoing acclimation to the new food supply (test solution). Initially, the BOD₅ value is seen to increase over the first few weekly tests. After about one month, it levels off, indicating the acclimation process is completed. The BOD₅ taken at this point is called an acclimated BOD₅.

All solutions tested in this work have exhibited a higher value for the acclimated than the unacclimated. In some instances the changes are relatively small, perhaps a 30 to 50 percent increase, while some are considerably larger.

In a municipal wastewater treatment system having secondary waste treatment such as activated sludge, there is a diverse population of bacteria. It is not necessary to introduce a specially acclimated bacteria population before discharging an effluent. The bacterial acclimation process will occur naturally as a new substance is introduced.

New processes generally involve a startup and test phase before gradually ramping up to full-scale production. Likewise, new materials or process chemicals are customarily tested on a small scale before being adopted for use. These phase-in tests create an effluent pattern to the POTW that is conducive to a gradual acclimation of the bacteria.

If a substance is known to be toxic to bacteria at concentrations that might realistically be encountered at the POTW, then it should not be disposed to the municipal sewer system. But, how many suppliers of chemicals and materials provide sufficient data on biodegradability so a fabricator can assess the environmental impact of a given disposal alternative? In the absence of data, there is a lot of guessing.

Assessing biodegradability

Compatibility of organic effluents with the bacterial system at the POTW can be largely demonstrated in laboratory tests known as electrolytic respirometry. This test procedure permits oxygen uptake by the bacteria to be monitored electronically. See Figure 1.

The end products of the bio-oxidation are carbon dioxide and water. Instead of using air as the oxygen source for the bacteria, a small water electrolysis cell mounted on top of the apparatus generates oxygen

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that feeds into the air space above the bacteria containing test solutions. The carbon dioxide is absorbed into a solution of caustic with the assistance of a wick. As the oxygen is absorbed into the solution, it creates a partial vacuum. This causes a shift in the level of the water electrolyte so electrical current can flow, thereby generating oxygen. As the pressure returns to atmospheric, the electrolyte solution shifts so it no longer contacts the electrodes. In this way, the electrical current, which is continuously recorded, directly correlates with oxygen demand. The volume of water generated has an inconsequential effect. The hydrogen generated at the cathode is dissipated harmlessly to atmosphere.

Acclimated bacteria are combined with sewer influent in one set of cells as a control. In additional cells run in parallel, the same acclimated bacteria and sewer influent are mixed with several predetermined concentrations of the test solution. The quantity of test solution is selected to be a percentage of the organic strength of the sewage. This may be varied for more concentrated effluents. The cumulative oxygen uptake or demand for each cell is plotted against time, generally over 20 to 21 days.

Since the quantities of acclimated bacteria and sewage are held constant within a given sample test series, any differences in oxygen uptake between the control and the unknown test solution can only be ascribed to the influence of that solution being evaluated. Further, this is the same process that normally occurs with bacteria degrading the sewage within the biological treatment system at the POTW. Therefore, any reduction in oxygen uptake for the samples containing the unknown test material indicates that it is interfering with the normal wastewater treatment process.

The shapes of cumulative oxygen demand curves compared to the control tell the story. See Figure 2. The bottom trace showing a rapid halt in further

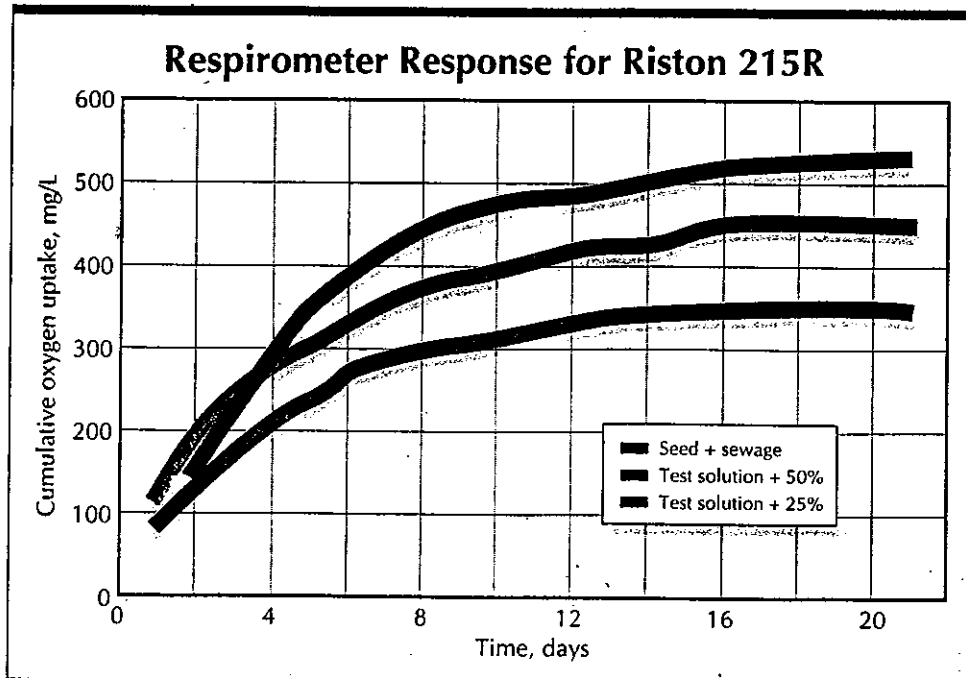
oxygen uptake indicates the test solution is toxic and has killed the bacteria. Not only is the substance being tested not biodegradable, but it halts the normal sewer process from functioning. If the cumulative oxygen uptake falls below the control, it demonstrates that the substance being tested exerts an inhibitory influence on the normal sewer use process. When the cumulative oxygen uptake is greater than the control, it verifies that the test material does not exert any toxic or inhibitory effects on the ability of the bacteria to function in degrading the sewage. Also, the incrementally higher oxygen uptake verifies that the test substance is undergoing biodegradation and provides a quantitative measurement.

Using electrolytic respirometry

Du Pont performed electrolytic respirometry testing for a variety of products used in PWB fabrication and assembly, including photopolymer films and processing chemicals in loaded developer and stripper solutions, photopolymer film solder masks in developers and monomer chemistry, cleaning agents, and electrodeposited resist. These all generate water-based effluents where the organic content and/or volume to be disposed justify this type of investigation. As seen in Figures 3 through 6, all of the effluents were sewer compatible. None exhibited toxic or inhibitory behavior on bacteria and all partially or fully biodegrade.

Electrolytic respirometry can be applied equally well to high organic strength effluents. For semi-aqueous processable photopolymers, proprietary processing chemistries are frequently used. These organic cosolvents are largely based on glycol butyl ethers and amines. Since the glycol ethers are such critical components for semi-aqueous processing and are the major contributors to organic strength in the effluent, they were also tested individually. Once

● Figure 5. The test solution contains equal amounts of developer and stripper, 6 to 7 percent organic cosolvents, and has a COD of several hundred thousand. The respirometry proceeds smoothly for the dose levels of the spent solutions adjusted to be 25 percent and 50 percent the BOD₅ of the sewage.



again, no evidence of toxic or inhibitory effects were observed on the bacteria for concentrations at which they would reasonably be anticipated in biological treatment at the POTW.

Other high organic strength compositions include a family of semi-aqueous cleaning agents introduced as replacements for ozone-depleting CFCs for cleaning PWBs following soldering and in metal cleaning. To accomplish the cleaning, the work is generally immersed in the cleaner. Following the cleaning step, the panels or parts are water rinsed. The organics, being almost totally water insoluble, phase separate and are recycled back to the main cleaning sump.

Small quantities of the cleaning agent remain in the water phase, usually several thousand ppm. In the preferred equipment configurations, most of this rinse water is also recycled. To retain the required cleanliness, several gallons of rinse water per hour should be purged out, which generates some wastewater effluent that has to be disposed.

Figure 6 shows the respirometer curves for this type of product. The differential oxygen uptake between the seed control (sewage) and the higher concentration (top curve) is less than twice the differential oxygen uptake between the seed control and the lower test concentration. When this type of behavior is observed, it points out that while the biodegradation at the lower concentration (950 ppm) gives the anticipated oxygen uptake, it does not at the higher concentration. This indicates that minor inhibition to biodegradation occurs at the higher concentration of 1900 ppm.

However, it should be clearly stated even at this concentration, no toxic effects occurred. As long as the concentration entering the biological wastewater treatment plant is maintained at 950 ppm or below, it will efficiently biodegrade. But it will not degrade with that same efficiency at 1900 ppm. So, small

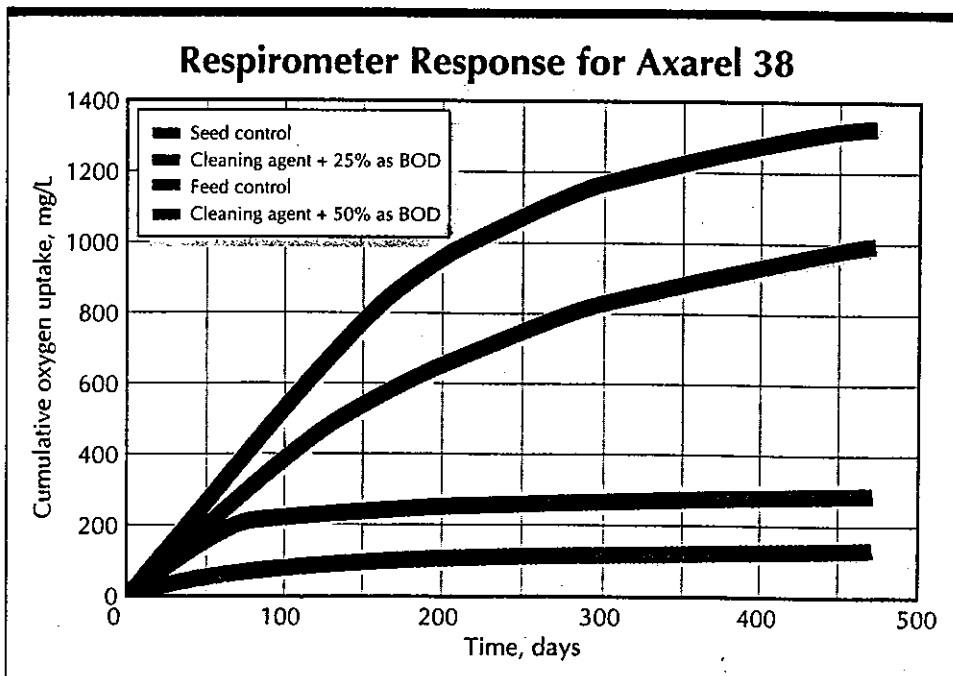
amounts of this product discharged to the sewer, as from a recycled rinse water purge, is fully acceptable. But the sewer is not a satisfactory disposal route for multigallon quantities. Incineration may be a better disposal option since the product has high thermal combustion values.

The high organic strength dosing characteristic leading to inhibition, as discussed above, is typical for all high-strength organic wastes. This same behavior exists for just about every organic substance as its concentration in the test solution is increased. Determining the concentration at which the inhibition occurs is essential for making a valid assessment of the upper concentration that such a substance can be safely discharged. Only in those instances where the combination of the organic strength and volume of that effluent being discharged could reduce the biodegradation efficiency, is testing at these elevated concentrations justified.

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Other measures of biodegradability

BOD/COD ratio provides important information on biodegradability. Chemical oxygen demand (COD) is a method of determining the organic strength of a material or solution by treating (oxidizing) it with hot dichromate solution and then determining the quantity of dichromate consumed. The units for COD are also expressed in mg/L of oxygen



● Figure 6. Both concentrations of cleaning agent test solution showed good oxygen uptake, but minor inhibition to biodegradation occurs at the higher concentration.

Initial study suggests most materials, excepting the polymers themselves, are largely biodegraded in the POTW.

demand. COD values vary in accordance with the inherent chemical structures being treated and their concentrations in the solution. For most pure organic substances, the COD ranges from 1.5 million to 2.5 million mg/L.

The BOD₅/COD ratio indicates the effectiveness or completeness with which a given waste biodegrades. If the BOD₅/COD ratio is 0.7 or higher, the waste is essentially totally biodegradable. When the ratios are 0.3 to 0.7, it indicates partial biodegradability. Spent aqueous photopolymer solutions typically show BOD₅/COD ratios in this range. Total biodegradability generally requires more than five days contact time with the bacteria. The polymeric materials that comprise the backbone of the photopolymer films are relatively slow to biodegrade and are partially broken down within the five-day test. When these same solutions are tested for BOD₂₀, appreciable biodegradation of these polymers occurs.

Some may argue the relevance of this since the average residence time for water flowing through a municipal biological system is 15 to 24 hours. For materials that are very highly water soluble, this may be the case. But in most instances the kinds of organic materials used in photopolymer films, cleaners, defoamers, etc., do not possess high water solubility. When introduced to an activated sludge biotreatment system, these organics will adsorb to the biomass allowing extended time for the biodegradation to take place. The typical residence times for sludge in a POTW is 5 to 20 days; therefore, BOD₅ and BOD₂₀ values have very pertinent significance.

Looking further downstream, many municipalities dispose of their sludge by agricultural land spreading. Much of the sludge is disposed by subsoil injection of a liquid concentrate. For the spent photopolymer solutions, initial study suggests that most materials excepting the polymers themselves are largely biodegraded in the POTW. The remaining polymeric material will continue to biodegrade under the aerobic conditions of moisture, bacteria and oxygen that exist in the soil.

Precipitating the dissolved photopolymers may be necessary in specific situations to meet rigid BOD₅ or COD effluent limits that typically exist for direct dischargers. But for most PWB manufacturers disposing to POTWs, precipitation may be superfluous and may not necessarily be environmentally advantageous. If the precipitated photopolymer material is incinerated, it is converted essentially to carbon dioxide and water. However, when the solids are disposed to a municipal landfill, they will not efficiently biodegrade under the prevailing anaerobic conditions and will contribute to the already existing burden of polymer materials in landfills.

While acid precipitated photopolymer solids (as-

suming it is correctly done) should not be RCRA hazardous wastes, some PWB manufacturers dispose them together with metal hydroxide sludges to hazardous waste landfills (also anaerobic). This seems to be a needless waste of this limited hazardous waste landfill capacity. Sometimes there is an option to precipitate RCRA listed metals together with the photopolymer precipitate. At this point a thorough assessment of regulatory considerations, costs, ease of operation and disposal, and long-term environmental assessment needs to be considered. And this is the point where corporate environmental posture needs to play a role.

Direct discharge

An entirely different set of considerations exist for direct dischargers whose spent effluents feed directly to a river, stream or lake. The efficient cleansing of the wastewater by biodegradation does not take place prior to the effluents reaching the water body. Tests in which effluents are evaluated using these higher life forms are called aquatic toxicity. Aquatic toxicity has been evaluated using daphne and fat head minnows with spent developers and strippers. The data indicate the test solutions exert a fairly toxic influence on these higher life forms. This verifies that spent developers and strippers must not be discharged directly to rivers and streams in the same concentrations at which they can safely be discharged to the POTW.

The discharge of small quantities of low organic strength photopolymer processing solutions may be possible. Most NPDES/SPDES permits governing direct discharges include a maximum limit on BOD₅ or COD, generally about 25 to 30 mg/L. As long as these concentra-

tions are not exceeded, the neutralized spent photopolymer solutions may be discharged assuming all other effluent parameters are below the permitted concentrations.

Some POTWs trying to assess and understand sources of aquatic toxicity in their own effluent occasionally want to test the aquatic toxicity of upstream dischargers. Such testing is not a rational approach for effluents that are dramatically changed by the bacterial digestion process.

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