future generating stations in or near the ocean, on bays, or along tidal rivers.

Water Pollution

EPA CONTRACTOR REPORT SAYS DIVERSITY INDICATES NEED FOR VARYING STANDARDS

The diversity of products and manufacturing operations indicates a need for separate effluent limitations for different segments within the organic chemicals industry, according to an Environmental Protection Agency contractor report.

The report, prepared by Roy F. Weston, Inc., solved the diversity problem by developing a process oriented categorization.

Weston's categories are as follows:

Category A, nonaqueous processes. In these processes, contact between water and reactants or products is minimal. Water is not required as a reactant or dilutent and is not formed as a reaction product. The only water usage stems from periodic washes or catalyst hydration. Heating and cooling are indirect or involve only nonaqueous fluids. Process raw waste loads should be virtually zero, with deviations caused only by spills or process upsets.

Category B, process water contact as steam dilutent and/or absorbent. Process water is in the form of dilution steam, direct product quench, or absorbent for effluent gases. Reactions are all vapor-phase over solid catalysts. Most processes have an absorber coupled with steam stripping of chemicals for purification and recycle. In some cases, it appears to be possible to reduce the raw waste load nearly to zero through increased recycle of contact water.

Category C, aqueous liquid-phase reaction systems. In these systems, reactions are liquid-phase with the catalyst in an aqueous medium. Continuous regeneration of the catalyst requires extensive water usage and substantial removal of spent inorganic by-products may be required. Additional water is involved in final purification or neutralization of products. Requirements for purging waste materials from the system could prevent the process raw waste load from approaching zero.

Category D, batch and semi-continuous processes. In these processes many reactions are liquid-phase with aqueous catalyst systems. Requirements for very rapid cooling necessitate provisions for direct addition of contact quench water or ice. Reactants and products are transferred from one piece of equipment to another by gravity flow, pumping, or pressurization. Much of the materials handling is manual and there is only limited use of automatic process control.

Filter presses and centrifuges are commonly used for solid-liquid separations and air or vacuum ovens are used for drying. Cleaning of noncontinuous production equipment constitutes a major source of waste water. Expected waste loads are at least 10 times those of comparable continuous processes.

The products and manufacturing processes included in category A are as follows:

Mixed aromatics with saturates–hydrogenation of pyrolysis gasoline from ethylene manufacture and naphtha reforming; mixed aromatics concentrate-solvent extraction; benzene-fractional distillation, toluene disproportionation, and toluene hydrodealkylation; and toluene-fractional distillation.

The category also included mixed xylenes (o-X, m-X, p-X, EB) fractional distillation and toluene disproportionation; ortho-xylene-fractional distillation; para-xylene-fractional distillation, isomerization, and crystallization and filtration; and petroleum naphthalene-fractional distillation and hydrorealkylation of alkyl napthalenes.

Others in the category were ethyl benzene-aklylation of benzene with ethylene; cumene-alkylation of benzene with propylene; cyclohexane-hydrogenation of benzene; phosgene-carbon monoxide and chlorine synthesis; ethyl chloride-hydrochlorination of ethylene and chlorination of ethane; and cyclopropane-extraction from liquified petroleum gas.

The products and manufacturing processes included in category B are as follows:

Ethylene-pyrolysis of hydrocarbons; propylene-pyrolysis of hydrocarbons; and butadiene-pyrolysis of hydrocarbons, dehydrogenation of N-butane, N-butylene (catalytic with steam dilution), catalytic oxidative dehydrogenation, and purification by extractive distillation.

Methanol-steam reforming of natural gas; ethanol-catalytic hydration of ethylene; isopropanol-catalytic hydration of propylene; acetone-dehydrogenation of isopropanol; maleic anhydride-air oxidation of benzene or butene; phthalic anhydride-air oxidation of ortho-xylene or naphthalene; acetaldehyde-oxidative-dehydration of ethanol; and acetylene-calcium carbide process, Wulff process, and BASF process.

Acetic anhydride-absorption of ketone in acetic acid; ethylene oxide-catalytic oxidation of ethylene; acrylonitrile-ammoxidation of propylene; formaldehyde-oxidation of methanol; acrylic acid-catalytic oxidation of propylene; and ethylene dichloride-oxychlorination of ethylene by hydrochloric acid and direct chlorination of ethylene.

Vinyl chloride-thermal cracking of ethylene dichloride and acetylene and anhydrous hydrochloric acid; ethyl ether-by-product of ethanol production via catalytic hydration of ethylene; isoprene-propylene dimerization/isomerization/cracking and dehydrogenation of isoamylene; and vinyl acetate-acetylene and acetic acid process and vapor phase ethylene and acetic acid process.

Mixed cresols and xylenols-phenol and methanol synthesis; methyl amines-methanol and ammonia reacted over dehydration catalyst; methyl halides-gaseous methanol and halogen acid passed through thermal converter; and dichlorodifluoromethane-reaction of hydrofluoric acid with chloroform.

Fluorinated hydrocarbons-reaction of hydrofluoric acid with carbon tetrachloride; trichlorotrifluoroethane-reaction of perchloroethylene and hydrofluoric acid; phthalates-reaction of phthalic anhydride and alcohol; and hexamethylenediamine-from adipic acid by reaction with ammonia followed by hydrogenation of adiponitrile, from butadiene, and from acrylonitile.

Urea-ammonia and carbon dioxide synthesis; acrolein-direct oxidation of ethylene; allyl chloride-high tempera-

ture chlorination of propylene; fatty acids-oxidation of nitrogen paraffins; and fatty amines-ammoniation of fatty acid followed by catalytic hydrogenation of aminonitriles.

Benzoic acid-air oxidation of toluene in L.P.; benzaldehyde-air oxidation of toluene V.P.; chloronaphthalenes-chlorination of naphthalenes; higher alcohols-high-pressure hydrogenolysis; methyl and ethyl acrylates-acetylene, nickel carbonyl, and methyl or ethyl alcohol; and trichloroethylene-catalytic-thermal dehydrochlorination of tetrachloroethane and chlorination of ethylene to 1,2 dichloroethane and conversion to T.C.E.

Tetrachloroethylene-chlorination of methane in atmosphere of carbon tetrachloride and high temperature chlorination of ethylene dichloride; chloroform-methane chlorination; methyl chloride-direct methane chlorination and esterification of methanol with hydrochloric acid; and P/O-dichlorobenzene-chlorination of chlorobenzene.

Glycerol-hydrolysis of epichlorohydrin with sodium hydroxide, catalytic hydrogenation of nigor, and from acrolein and isopropanol; hexamethylene tetramine-ammonia plus formaldehyde; decahydronaphthalene-hydrogenation of naphthalene; carbon tetrachloride-chlorination of carbon disulfide and from chlorinated methanes production; carbon bisulfide-sulfur and methane and sulfur and charcoal in electric arc furnace; and benzene hexachloride-benzene chlorination in presence of actimic light.

Liquid Phase Reaction Systems

The products and manufacturing processes included in category C are as follows:

Ethanol – sulfuric acid hydrolysis of ethylene; isopropanol – sulfuric acid hydrolysis of propylene; acetone – cumene oxidation with cleavage of hydroperoxide in sulfuric acid; and phenol – Raschig process, chlorobenzene process, sulfonation process, and cumene oxidation with cleavage of hydroperoxide in sulfuric acid.

Oxo-chemicals, including N-butyl alcohol, isobutyl alcohol, 2-ethylhexanol, isooctyl alcohols, and decyl alcohols – carbonylation and condensation; acetaldehyde – ethylene oxidation via Wacker process; and acetic acid – oxidation of liquified petroleum gas (butane), oxidation of acetaldehyde, and carbonylation of methanol.

Methyl ethyl ketone – sulfuric acid hydrolysis of butene-2 and dehydrogenation of sec-butanol and oxidation of liquified petroleum gas (butane), by-product of acetic acid manufacture; methyl methacrylate – acetone cyanohydrin process; and ethylene oxide – chlorohydrin process.

Acrylonitrile – acetylene-HCN process; ethylene glycol – sulfuric acid catalyzed hydration of ethylene oxide; acrylic acid – carbon monoxide synthesis with acetylene; and ethyl acrylate – acetylene and ethanol in presence of nickel carbonly catalyst, oxidation of propylene to acrylic acid followed by esterification, and reaction of ketone with formaldehyde followed by esterification.

Styrene monomer – alkylation of benzene with ethylene and dehydrogenation of ethylbenzene with steam; adipic acid – oxidation of cyclohexane/cyclohexanol/cyclohexanone and direct oxidation of cyclohexane with air; and terephthallic acid – oxidation of para-xylene with nitric acid and catalytic oxidation of para-xylene.

Dimethyl terephthalate – esterification of TPA with methanol and sulfuric acid and vapor phase methylation of phenol; paracresol – oxidation of para-cymene with cleavage in sulfuric acid; cresylic acids – caustic extraction from cracked naphtha; and aniline – nitration of benzene with nitric acid (L.P.) and hydrogenation of nitrobenzene.

Chloroprene – dimerization of acetylene to vinyl acetylene followed by hydrochlorination and vapor phase chlorination of butadiene followed by isomerization and reaction; bis-phenol-a – condensation of phenol and acetone in presence of hydrochloric acid; and propylene oxide – addition of propylene and carbon dioxide to aqueous calcium hypochlorite and liquid phase oxidation of isobutante followed by liquid phase expoxidation.

Propylene glycol – hydration of propylene oxide catalyzed by dilute sulfuric acid; vinyl acetate – liquid phase ethylene and acetic acid process; anthraquinone – catalytic air oxidation of anthracene; beta naphthol – naphthalene sulfonation and caustic fusion; and caprolactam – hydroxyl amine production, cyclohexanone production, cyclohexanone oximation, oxime rearrangement, purification, and ammonium sulfate recovery.

Toluene di-isocyanate – toluene nitrification, toluene diamine production, hydrochloric acid electrolysis, phosgene production, TDI production, and purification; silicones – reaction of silicon metal with methyl chloride; and naphthemic acids – from gas-oil fraction of petroleum by extraction with caustic soda solution and acidification.

Ethyl cellulose – from alkali cellulose and ethyl chloride or sulfate; cellulose acetate – acetylation of cellulose with acetic acid followed by saponification with sulfuric acid for diacetate; chlorobenzene – Raschig process; chlorophenol – direct chlorination of phenol and from chloroaniline through diazonium salt; and chlorotoluene – catalytic chlorination of toluene.

Hydroquinone – oxidation of aniline to quinone followed by hydrogenation; naphthosulfonic acids – sulfonation of B-naphthol and caustic fusion of naphthalene sulfonic acid; nitrobenzene – benzene and nitric acid in presence of sulfuric acid; and amyl acetate – esterification of amyl alcohol with acetic acid.

Amyl alcohol – pentane chlorination and alkaline hydrolysis; ehtyl ether – dehydration of ethyl alcohol by sulfuric acid; ethyl butyrate – esterification of ethyl alcohol with butyric acid; ethyl formate – esterification of ethyl alcohol with formic acid; and tetraethyl lead – reduction of ethyl chloride with amalgam of sodium and lead.

Formic acid – sodium hydroxide and carbon monoxide; methyl isobutyl ketone – dehydration of acetone alcohol to mesityl oxide followed by hydrogenation of double bond; napthol – high-temperature sulfonation of naphthalene followed by hydrolysis to B-naphthol; and pentachlorophenol – chlorination by phenol.

Sodium pentachlorophenate – reaction of caustic soda with pentachlorophenol; toluidines – reduction of nitrotoluenes with iron and sulfuric acid; hydrazine – indirect oxidation of ammonia with sodium hypochlorite; oxalic

acid – sodium formate process; oxalates – sodium formate process; and sebacic acid – caustic hydrolysis of ricinoleic acid.

Glycerol – acrolein epoxidation/reduction followed by hydration and propylene oxide to allyl alcohol followed by chlorination; diethylene glycol diethyl ether – ethylene glycol and ethyl alcohol condensation dehydration; and DDT – monochlorobenzene and chloral in presence of sulfuric acid.

Pentachloroethylene – chlorination of acetylene; methylene chloride – methane chlorination and methanol esterification followed by chlorination; pentaerythritol – acetaldehyde and formaldehyde in presence of basic catalyst; chloral – chlorination of acetaldehyde; and triphenyl phosphate – phenol and phosphorous oxychloride.

Tridecyl alcohol – from propylene tetramer; tricresyl phosphate – cresylic acid and phosphorous oxychloride; amil alcohol – chlorination of pentanes and hydrolysis of amyl chlorides; acrylamide – acrylonitrile hydrolysis with sulfuric acid; higher alcohols – sodium reduction process; and synthetic amino acids – acrolein and mercaptan followed by treatment with sulfuric acid and sodium cyanide.

Organic esters – alcohol and organic acid, sulfuric acid catalyst; trialkylacetic acids – olefins and carbon monoxide followed by hydrolysis; fatty acids – batch or continuous hydrolysis; lauric acid esters – esterification of lauric acid; and oleic acid esters – esterification of oleic acid.

Acetophenone – by-product of phenol by cumene peroxidation; acrolein – condensation of acetaldehyde with formaldehyde; ethylacetate – acetic acid and ethyl alcohol in presence of sulfuric acid; propyl acetate – acetic acid and propyl alcohol in presence of sulfuric acid; and acetin – glycerol and acetic acid.

Propionic acid – carbonylation of ethyl alcohol with carbon monoxide at high pressure and oxidation of propionaldhyde; fatty alcohol – reduction of fatty acid with sodium metal and high pressure catalytic hydrogenation of fatty acids; butyl acetate – esterification of acetic acid and butyl alcohol in presence of sulfuric acid; and sec-butyl alcohol – hydrolysis of butylene in sulfuric acid with steam.

N-butyl alcohol – condensation of acetaldehyde to crotonaldehyde followed by hydrogenation; n-butyl propionate – esterification of propionic acid with butyl alcohol in sulfuric acid; chloroacetic acid – chlorination of acetic acid; sodium chloroacetate – esterification of chloroacetic acid; and chloropicrin – picric acid and calcium hypochlorite and nitrification of chlorinated hydrocarbons.

Thioglycolic acid – monochloroacetic acid and hydrogen sulfide followed by neutralization; adiponitrile – adipic acid and ammonia; sodium benzoate – benzoic acid neutralized with sodium bicarbonate; sodium sulfoxalate formaldehyde – zine hydrosulfite, formaldehyde, and caustic soda; sodium acetate – neutralization of acetic acid with caustic soda; and tartaric acid – maleic anhydride and hydrogen peroxide.

Isocyanates – phosgene and amines and coal tar cyclic intermediates – coal tar distillation.

Batch Processes

The products and manufacturing processes included in category D are as follows:

Coumarin – heating salicylic aldehyde, sodkum acetate, and acetic anhydride; resorcinal – fusing benzene-meta-disulfonic acid with sodium hydroxide; phosphotungstic acid lakes – precipitation of basic dyestuffs with solutions of phosphotungstic acid; and methyl violet – derivatives of paranosaniline.

Lake red – coupling 2-chloro-5-aminotoluene-4-sulfonic acid with B-naphthol; lithol rubine – diazotization of p-toluidine meta sulfonic acid followed by coupling with 3-hydrophy-2-naphthic acid; and eosin toners – bromination of fluorescin.

Amino anthraquinone – reduction of nitroanthraquinon and substitution of sulfonate with amino group; amino azobenzene (para) – catalytic heating of diazoaminobenzene and aniline solution and aniline hydrochloride; and aminoazotoluene (ortho) – from o-toluidine by treatment with nitrite and hydrochloric acid.

Amino phenol (O, M, P) – (meta) fusion of sulfanilic acid with sodium hydroxide and ether extraction, (ortho) sodium hydroxide reduction of O-nitrophenol and aqueous ammonia, (para) reduction of p-nitrophenol by iron and hydrochloric acid, and electrolytic reduction of nitrobenzene in sulfuric acid.

Anthraquinone (dyes) – heating phthalic anhydride and benzene in presence of aluminum chloride catalyst and dehydrating; azine dyes – from phenazine; azobenzene – reduction of nitrobenzene with sodium stannite; azo dyes (generic) – diazotation and coupling; and monosodium glutamates – fermentation of carbon source and acrylonitrile oxoreaction, strecher reaction, and hydrolysis.

Flavors – rectification of sulfate turpentine and pyrolysis of terpenes and extraction from natural stuffs; camphor, synthetic – pinene to camphene followed by treatment with acetic acid and nitrobenzene; and citral – separate from lemon grass oil by fractional distillation.

Citric acid – mold fermentation of carbohydrates; lime citrate (calcim citrate) – by-product production of citric acid; citronellol – extraction from oils of citronella, geranium, and rose; peacock blue – lake of acid glaucine blue dye on alumina hydrate; and O/P nitrophenol – caustic fusion of p-nitrochlorobenzene and dilute nitric acid and phenol at low temperature.

Vanillin – extraction from lignin; diphenylamine – reaction of aniline hydrochloride with aniline; alkylated diphenylamines – alkylation of diphenylamine obtained by reaction of aniline hydrochloride with aniline; and ethyl nitrite – ethyl alcohol and alkali nitrites and sulfuric acid.

Ferric ammonium oxalate – ammonium linoxalate and ferric hydroxide; calcium oxalate – sodium oxalate and lime; calcium stearate – sodium stearate and calcium chloride; methyl salicylate – methanol and salicylic acid in presence of sulfuric acid; and calcium tartrate – reaction of calcium salt and crude cream of tartar.

Alkylated phenols – alkylation with lewis acid catalyst; acetamide – distillation of ammonium acetate; organic esters – steam distillation of naturally occuring esters; nitroaniline – p-nitrochlorobenzene and ammonia; and sorbitol – hydrogenation of fructose-free glucose.

Terpineol – hydration of pinene; saccharin – from o-toluene sulfonamide and from phthalic anhydride via anthranilic acid; tannic acid – extraction of powdered nutgalls; and algin (sodium alginate) – extraction from brown algae; and mustard gas (dichlorodiethyl sulfide) – ethylene and sulfur chloride and thyoglycol and hydrogen chloride.

Ionone – condensation of citronellal from lemon-grass oil with acetone; geraniol – from geranium oil, citronellal, and palmarose and from myrcene; sodium citrate – sodium sulfate and calcium citrate.

Calcium citrate – by-product in manufacture of citric acid; cream of tartar (potassium bitartrate) – from argols by extraction with water; dimethyl hydrazine – dimethylamine and chloramine, dimethylamine and sodium nitrite followed by reduction, and catalytic oxidation of dimethylamine and ammonia; and nitrophenol – nitrochlorobenzene and caustic soda.

The Weston report said that although it is not possible to develop a total suspended solids limitation related directly to production, a practical upper limit associated with effluent limitations of best practicable control technology can be set.

This limit is as follows:

Category	Total Suspended Solids mg/L
A	50
B	50
C	170
D	50

Weston said that these values should only be used as guidelines and that any specific limitations should consider both the specific requirements for removal of dissolved organics and the associated biological solids limits required to accomplish such removal.

The treatment systems upon which effluent limitations for best available control technology and new source performance standards were based all involve a filtration step. The total suspended solids concentration in the effluent is expected to be 15-20 mg/L.

The effluent limitation developed for five-day biological oxygen demand, carbon oxygen demand, and total organic carbon within each category consider flow and pollutant loadings. Although no values were specified for flow, the amount of allowable discharge increased with the flow.

Implicit in in-process best practicable technology was segregation of noncontact waste waters from process waste water for continuous processes. Process waters are recycled in quantities such that the total contact waste water discharged does not exceed 3,000 gallons/1,000 pounds of product for categories A, B, and C. The batch process waste waters from category D include cooling water and subsequently have waste water flows ranging from 10,000 to 100,000 gallons/1,000 pounds of product.

Best practicable end-of-pipe technology was based on the application of a single-stage activated sludge treatment system. The system is applicable to all of the categories. It is preceded by an equalization basin to contain storm run-off and smooth out raw waste load variations. The equalization basin is equipped with an oil skimmer and provision for pH control. There are no primary clarifiers, as the suspended solids limit in the raw waste load are generally under 100 mg/L.

The final clarifiers have a flocculation compartment with provision for the addition of coagulants, so that total suspended solids limits in the effluent generally can be maintained between 50-170 mg/L. Mixed liquid suspended solids concentrations in the aeration basins can be as high as 2,000-7,000 mg/L when treating some of the highly concentrated wastes from category C.

Nonwater Quality Aspects

The major nonwater quality consideration which may be associated with in-process control measures is the use of and alternative means of ultimate disposal, according to the report.

The report said that alternative disposal techniques, such as incineration, ocean discharge, and deep-well injection are feasible. However, recent regulations tend to limit applicability of ocean discharge and deep-well injection because of potential long-term detrimental effects.

Incineration is a viable alternative, particularly for waste streams associated with category C. Associated air pollution and need for auxiliary fuel, depending on the heating value of the waste, are considerations which must be evaluated on an individual basis of each use.

Other nonwater quality aspects, such as noise limits, will not be perceptibly affected.

Water Pollution

EPA CONTRACTOR RECOMMENDS STANDARDS FOR BUILDING PAPER, ROOFING FELT FIRMS

Effluent limitations and standards of performance for the building paper and roofing felt segment of the builders paper and board industry were recommended by WAPORA, Inc., under an Environmental Protection Agency contract.

EPA had the report prepared in compliance with sections 304 (b) and 306 of the Federal Water Pollution Control Act Amendments of 1972.

The Act requires that effluent limitations guidelines set forth the degree of effluent reduction attainable through application of best practicable control technology currently available by July 1, 1977 and best available technology economically achievable by July 1, 1983.

The Act further requires that new source performance standards set forth the degree of effluent reduction which is achievable through application of best available demonstrated control technology, processes, operating methods, or other alternatives.

WAPORA's proposed guidelines recognized biological waste treatment as the base technology for 1977 and major internal mill improvement and biological waste treatment as the base control and treatment technologies for both existing and new mills in 1983.

The recommended effluent limitations guidelines and

