Chemical Information Review Document

for

Diazonaphthoquinone Derivatives Used in Photoresists

Sodium 1,2-naphthoquinone-2-diazide-5-sulfonate [2657-00-3]
1,2-Naphthoquinone-2-diazide-5-sulfonyl chloride [3770-97-6]
2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) [5610-94-6]
2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate [68510-93-0]

Supporting Nomination for Toxicological Evaluation by the National Toxicology Program

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National Toxicology Program
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Abstract

Workers involved in the manufacture of semiconductors are exposed to photoresists, some of which contain a diazonaphthoquinone (DNQ) derivative as the photoactive component. Four commercially available DNQ compounds used in the manufacture or formulation of photoresists are listed on the Toxic Substances Control Act Inventory: sodium 1,2-naphthoquinonediazide-5-sulfonate, 1,2-naphthoquinonediazide-5-sulfonyl chloride, 2,3,4-trihydroxy-benzophenone tris(1,2-naphthoquinonediazide-5-sulfonate), and 2,3,4-trihydroxybenzo-phenone 1,2-naphthoquinonediazide-5-sulfonate. Under the 1986, 1990, 1994, 1998, and 2002 Inventory Update Rule, an aggregate production volume ranging between 10,000 lb and 500,000 lb was reported for sodium 1,2-naphthoquinone-2-diazide-5-sulfonate, 1,2-naphthoquinone-2-diazide-5-sulfonyl chloride, and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate. DNQ derivatives can be released into the wastewater of manufacturing plants that produce photoresist material. The acute toxicity of 1,2-naphthoquinonediazide-5-sulfonyl chloride in mice and rats was low. It was a moderate eye irritant in rabbits but a potent skin sensitizer in guinea pigs. Given as a mixture in alcohol:glycerine to guinea pigs for ten days, it produced moderate to strong erythema associated with slight to moderate edema and numerous raised eschars. In a short-term rat study, 1,2-naphthoquinonediazide-5-sulfonyl chloride increased weight gain, mean hemoglobin concentrations, hematocrit, white blood cell counts, and slight elevations in serum levels of glutamic oxalacetic transaminase, lactic dehydrogenase, alkaline phosphatase, and urea nitrogen. Additionally, the mean liver weights of treated animals were slightly lower than controls. No other toxicological data were available.

Executive Summary

Basis for Nomination

Workers involved in semiconductor device fabrication are potentially exposed to photoresists during photolithography processes. Results from laboratory as well as epidemiological studies provide some evidence of adverse reproductive effects associated with exposure to photoresist mixtures or their individual chemical constituents. Positive photoresist mixtures commonly used in 365 nm (I-line) lithography contain a diazonaphthoquinone (DNQ) derivative as the photoactive compound. The following commercially available DNQ compounds were identified as being used in the manufacture or formulation of photoresists: sodium 1,2-naphthoquinonediazide-5-sulfonate; 1,2-naphthoquinonediazide-5-sulfonyl chloride; 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate); and 2,3,4-trihydroxy-benzophenone 1,2-naphthoquinonediazide-5-sulfonate. The DNQ derivatives sodium 1,2-naphthoquinonediazide-5-sulfonate, 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinone-diazide-5-sulfonate), and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate were nominated by the National Institute of Environmental Health Sciences (NIEHS) for toxicological characterization based on moderate production and use and the lack of adequate toxicological data. 1,2-Naphthoquinonediazide-5-sulfonyl chloride is not being considered for study due to its flammable and irritant properties.

Nontoxicological Data

The sensitizers for the positive photoresists are usually the derivatives of DNQ. DNQ sulfonates, which are soluble in organic solvents and insoluble in aqueous alkaline solutions, undergo a number of reactions on exposure to light, ultimately resulting in the formation of substituted indene carboxylic acid. This acid, unlike the starting DNQ, is readily soluble in aqueous alkaline solutions. The five-substituted derivatives of DNQ were found to be the best for preparing the positive photoresists.

Commercial Availability: Sodium 1,2-naphthoquinonediazide-5-sulfonate is supplied by the following U.S. companies: ChemDesign Corporation (Fitchburg, MA); MRI International (Newton, NJ); ChemPacific USA Sales Marketing and Research Center (Baltimore, MD); Fluka Chemical Corporation (Ronkonkoma, NY); Pfaltz and Bauer, Inc. (Waterbury, CT); Monomer-Polymer and Dajack Laboratories, Inc. (Feasterville, PA); and TCI America (Portland, OR). Under the 1998 and 2002 Inventory Update Rule (IUR), Specialty Chemical Products Corporation was listed as a company manufacturing or importing sodium 1,2-naphthoquinonediazide-5-sulfonate. It is also produced by Esprix Technologies (Sarasota, FL) as Diazo 10. PC Associates Inc. (Livingston, NJ) is a manufacturer and world-wide distributor of the salt (monohydrate).

1,2-Naphthoquinonediazide-5-sulfonyl chloride is supplied by Pfaltz and Bauer, Inc., ChemDesign Corporation, MRI International, and TCI America. Under the 1998 and 2002 IUR, ChemDesign Corporation and Arch Chemicals, Inc. were listed, respectively, as companies manufacturing or importing the compound and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate. No producers or suppliers were found for 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate).

Production and Import Volumes: Under the 1986, 1990, 1994, 1998, and 2002 Inventory Update Rule (IUR), an aggregate production volume ranging between 10,000 lb (4535.9 kg) and 500,000 lb (226,800 kg) was reported for sodium 1,2-naphthoquinone-2-diazide-5-sulfonate, 1,2-naphthoquinone-2-diazide-5-sulfonyl chloride, and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate. In 1986 and 1990, the same range was reported for 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinone-diazide-5-sulfonate).

Uses: The majority of positive DNQ/novolak photoresists use mixtures of various DNQ-esters and positional isomers as the photoactive compounds. The five-substituted derivatives of DNQ were found to

be the best for preparing the positive resists. 2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate are ingredients in numerous photoresist compositions from Hoechst-Celanese Corporation and Clariant Corporation. Additionally, sodium 1,2-naphthoquinonediazide-5-sulfonate is a component of a polymer film for use as a near-field write-once memory medium and is used in the manufacture of presensitized printing plates and in the photosensitive layer for the production of waterless lithographic printing plate master. 1,2-Naphthoquinonediazide-5-sulfonyl chloride is also manufactured for lithographic applications. Numerous Japanese patents exist for the compound. It is a component of radiation-sensitive resin compositions for positive-working resists, semiconductor device fabrication, and for the manufacture of electronic parts.

Environmental Occurrence and Persistence: Total organic carbon from raw industrial wastewater from large-scale integrated circuit photoresist processing, containing 1,2-naphthoquinone-2-diazido-5-sulfonic acid sodium salt as a main component with high sodium chloride concentration (>20 kg/m^3 [>2%]), was removed by treatment with hydrogen peroxide and ultraviolet (UV) irradiation, resulting in complete mineralization of the organic compounds. The use of chlorine or sodium hypochlorite and hydrogen peroxide in a second step was found to successfully treat wastewaters containing the salt. In the wastewater from a Japanese plant producing negative photoresist material, anaerobic digestion using microbes separated from soils and sludges decomposed >98% within four days, but degraded only 10% of the derivatives formed by oxidation and photochemical decomposition within 24 days.

Regulatory Status: The four DNQ derivatives in this report are listed on the Toxic Substances Control Act (TSCA) Inventory. Sodium 1,2-naphthoquinonediazide-5-sulfonate, at a concentration of 100%, is also on the list of self-reactive materials authorized for transportation and not subject to the approval provisions in Section 173.124(a)(2)(iii) (49 CFR 173.224). Under the dangerous goods regulation of the International Maritime Organization, the compound is not accepted in self-reactive solid type D substances (UN No. 3226).

Under the Superfund Amendments and Reauthorization Act (SARA) Title III Sections 311-312 (40 CFR 370.21), 1,2-naphthoquinonediazide-5-sulfonyl chloride is not an acute or chronic health hazard, and no sudden releases are expected. It is, however, a flammable and reactive hazard. The substance is also subject to disposal regulations (40 CFR 262 [Hazardous Waste Numbers: D001, D003]) and transportation regulations (40 CFR 172.101 [proper shipping name: Self-reactive solid type B; UN No. 3222]).

Under SARA Title III Sections 311-312 (40 CFR 370.21), 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate are not hazards in the following categories: acute or chronic health, fire, reactive, and sudden release. Under the International Maritime Dangerous Goods (IMDG) code, both have a UN number of 3226.

Human Data

Exposure to the DNQ derivatives may occur during the manufacture and use of products containing the compounds, particularly photolithography processes in the microelectronics industry. No specific information regarding workplace exposures to the DNQ derivatives was available. Acute or short-term exposure with 1,2-naphthoquinonediazide-5-sulfonyl chloride may be irritating to the skin and the eyes.

Toxicological Data

The only toxicological data located was for 1,2-naphthoquinonediazide-5-sulfonyl chloride. No data regarding chemical disposition, metabolism, and toxicokinetics; chronic exposure; synergistic or

antagonistic effects; cytotoxicity; reproductive or teratological effects; carcinogenicity; or genotoxicity were available.

Acute Toxicity: An oral LD_{50} value of >3200 mg/kg (11.91 mmol/kg) body weight was reported for 1,2-naphthoquinonediazide-5-sulfonyl chloride in both rats and mice. Intraperitoneal (i.p.) LD_{50} values of 400 mg/kg (1.49 mmol/kg) and 200 mg/kg (0.744 mmol/kg), respectively, were calculated. 1,2-Naphthoquinonediazide-5-sulfonyl chloride was a moderate skin irritant in guinea pigs and a moderate eye irritant in rabbits.

Short-term or Subchronic Toxicity: 1,2-Naphthoquinonediazide-5-sulfonyl chloride, incorporated (50% w/v) into a mixture of alcohol:glycerine (1:9 v/v) and applied to the clipped backs of guinea pigs at a rate of 0.5 mL/pig/day for ten days produced moderate to strong erythema associated with slight to moderate edema and numerous raised eschars.

Male Charles River CD, COBS outbred rats fed 1,2-naphthoquinonediazide-5-sulfonyl chloride (0.1% or 1.0% w/w [up to 1000 mg/kg/day]) for 11 days had increased weight gain, mean hemoglobin concentrations, hematocrit, white blood cells, as well as slightly elevated serum levels of glutamic oxalacetic transaminase, lactic dehydrogenase, alkaline phosphatase, and urea nitrogen. The mean liver and mean relative liver weights of the test animals were slightly lower than controls.

Immunotoxicity: 1,2-Naphthoquinonediazide-5-sulfonyl chloride (dose and duration not provided) was a potent skin sensitizer in guinea pigs. The animals were sensitized with injection of a compound-heparinized-whole-rabbit-blood reaction product into the footpads; subsequent challenge was by topical application of a solution of the compound.

Structure-Activity Relationships

Many other DNQ derivatives were identified, most of apparent little commercial importance. A gavage LD_{50} value of 8125 mg/L was reported for 1,2-naphthoquinonediazide-5-sulfonic acid [4857-48-1] in rats. Using the MultiCASE expert system to predict estrogen receptor binding capacity of a series of compounds, 1-diazonaphthoquinone-4-sulfonic acid [4857-47-0 or 887-76-3] was found to be inactive. No toxicity data were available for any of the other compounds.

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1.0 Basis for Nomination

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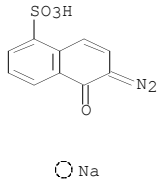
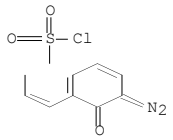
2.0 Introduction

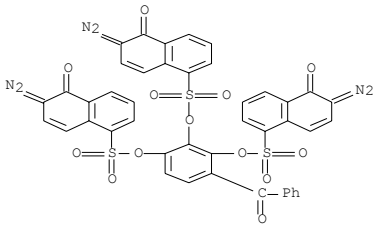
Sodium 1,2-naphthoquinonediazide-5-sulfonate
[2657-00-3]



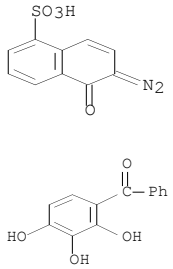
1,2-Naphthoquinonediazide-5-sulfonyl chloride
[3770-97-6]



2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)
[5610-94-6]



2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate
[68510-93-0]



The CASRN for 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate may be considered generic for the following isomers:

- 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate);
- 2,3,4-trihydroxybenzophenone 4-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate);
- 2,3,4-trihydroxybenzophenone 3-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate;
- 2,3,4-trihydroxybenzophenone 2-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate);

- 2,3,4-trihydroxybenzophenone 3,4-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate;
- 2,3,4-trihydroxybenzophenone 2,3-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate; and
- 2,3,4-trihydroxybenzophenone 2,4-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate).

2.1 Chemical Identification and Analysis

2.1.1 Sodium 1,2-naphthoquinonediazide-5-sulfonate

Sodium 1,2-naphthoquinonediazide-5-sulfonate ([$C_{10}H_6N_2O_4S$•Na]; mol. wt. = 273.24) is also called:

NA 125
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo, sodium salt (7CI, 8CI, 9CI)
Sodium 1,2-naphthoquinone-2-diazide-5-sulfonate
Sodium 2,1-diazonaphthol-5-sulfonate
Sodium 2-diazo-1-hydroxynaphthalene-5-sulfonate
Sodium 2-diazo-1-naphthol-5-sulfonate
Sodium 2-diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonate

Sources: IMO (undated); Registry (2002)

2.1.2 Sodium 1,2-naphthoquinonediazide-5-sulfonyl chloride

1,2-Naphthoquinonediazide-5-sulfonyl chloride ([$C_{10}H_5ClN_2O_3S$]; mol. wt. = 268.68) is also called:

1-Hydroxy-5-chlorosulfonyl-2-naphthalenediazonium hydroxide, inner salt
1-Naphthalenesulfonyl chloride, 6-diazo-5,6-dihydro-5-oxo (6CI, 7CI, 8CI, 9CI)
1,2-Naphthoquinone-2-diazide-5-sulfonyl chloride
1,2-Naphthoquinonediazido-5-sulfonyl chloride
1-Oxo-1,2-dihydro-2-diazonaphthalene-5-sulfonyl chloride
1-Oxo-2-diazonaphthoquinone-5-sulfonyl chloride
2-Diazo-1-naphtho-5-sulfonyl chloride
2-Diazo-1-naphthol-5-sulfonyl chloride
2-Diazo-1-naphthone-5-sulfonic acid chloride
2-Diazo-1-naphthone-5-sulfonyl chloride
2-Diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonyl chloride
2-Diazo-1-oxonaphthalene-5-sulfonyl chloride
2-Diazo-1(2*H*)-naphthalenone-5-sulfonyl chloride
2-Diazo-1,2-dihydro-1-oxonaphthalene-5-sulfonyl chloride
2-Diazo-1,2-naphthoquinone-5-sulfonyl chloride
3-Diazo-4-oxo-1-naphthalenesulfonyl chloride
5-(Chlorosulfonyl)-1,2-naphthoquinone-2-diazide
6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonyl chloride
6-Diazo-5,6-dihydro-5-oxonaphthalene-2-sulfonyl chloride
6-Diazo-5-hydroxy-1-naphthalenesulfonyl chloride
6-Diazo-5-oxo-1-naphthalenesulfonyl chloride
Naphthoquinone-(1,2)-diazido-(2)-5-sulfonyl chloride
o-Naphthoquinonediazide-5-sulfonyl chloride

Sources: MSDS-OHS (2001a); Registry (2002)

2.1.3 2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)

2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) ([$C_{43}H_{22}N_6O_{13}S_3$]; mol. wt. = 926.88) is also called:

Benzophenone, 2,3,4-trihydroxy-, tris(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) (8CI)
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo, 4-benzoyl-1,2,3-benzenetriyl ester (9CI)
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, triester with 2,3,4-trihydroxybenzophenone (7CI, 8CI)
2,1,5-Diazonaphthoquinone ester with 2,3,4-trihydroxybenzophenone
2,3,4-Trihydroxybenzophenone 1,2-naphthoquinone-2-diazide-5-sulfonic acid triester
2,3,4-Trihydroxybenzophenone naphthoquinone-1,2-diazide-5-sulfonic acid ester (1:3)
2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinone-2-diazide-5-sulfonate)
2,3,4-Tris(1,2-naphthoquinone-2-diazido-5-sulfonyloxy)benzophenone
2,3,4-Tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)benzophenone
6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonic acid, 4-benzoyl-1,2,3-benzenetriyl ester
6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonic acid, triester with 2,3,4-trihydroxybenzophenone
NT 300
NT Ester-5-sulfonic acid
PAC III

Sources: MSDS-OHS (2001b); Registry (2002)

2.1.4 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate

2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate ([$C_{13}H_{10}O_4$ x $C_{10}H_6N_2O_4S$]; mol. wt. = 250.25) is also called:

1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with phenyl(2,3,4-trihydroxyphenyl)methanone (9CI)
1,2-Naphthoquinonediazido-5-sulfonyl chloride 2,3,4-trihydroxybenzophenone ester
2,1,5-Diazonaphthoquinone sulfonic acid, ester with 2,3,4-trihydroxy benzophenone
2,3,4-Trihydroxybenzophenone 1,2-naphthoquinone-2-diazide-5-sulfonate
2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazido-5-sulfonate
2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonic acid ester
2,3,4-Trihydroxybenzophenone 1-naphthoquinone-2-diazide-5-sulfonyl chloride ester
2,3,4-Trihydroxybenzophenone ester with 1,2-naphthoquinonediazide-5-sulfonic acid
2,3,4-Trihydroxybenzophenone ester with 1,2-naphthoquinonediazido-5-sulfonyl chloride
2,3,4-Trihydrodroxybenzophenone ester with naphthoquinone-1,2-diazido-5-sulfonyl chloride (1:2:5)
2,3,4-Trihydroxybenzophenone naphthoquinone-(1,2)-diazide-(2)-5-sulfonic acid ester
2,3,4-Trihydroxybenzophenone naphthoquinone-1,2-diazido-5-sulfonate
2,3,4-Trihydroxybenzophenone *o*-naphthoquinonediazide-5-sulfonyl chloride ester
2,3,4-Trihydroxybenzophenone-1,2-naphthoquinonediazido-5-sulfonic acid ester
2,3,4-Trihydroxybenzophenone-1-oxo-2-diazonaphthoquinone-5-sulfonate
NOD
NT 200
THBP 215

Sources: MSDS-OHS (2001c); Registry (2002)

2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and the six other possible 2,1-diazonaphthoquinone-5-sulfonates of 2,3,4-trihydroxybenzophenone have been

isolated and characterized by infrared (IR), chromatography (e.g., high-performance liquid chromatography [HPLC]), and advanced nuclear magnetic resonance (NMR) techniques (DiCarlo et al., 1994).

2.2 Physical-Chemical Properties

Property	Information	Reference(s)
	1,2-Naphthoquinonediazide-5-sulfonyl chloride	
Physical State	orange solid	MSDS-OHS (2001a)
Odor	odorless	MSDS-OHS (2001a)
Decomposition Point (^{o}C)	100	MSDS-OHS (2001a)
	113	Chinamarket (1998)
Soluble in:	dioxane and acetone	Chinamarket (1998)
Insoluble in:	water	Chinamarket (1998)
	2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)	
Physical State	solid or powder	MSDS-OHS (2001b)
	2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate	
Physical State	liquid	MSDS-OHS (2001c)

1,2-Naphthoquinonediazide-5-sulfonyl chloride is a flammable solid; dust or air mixtures of the substance may ignite or explode. The compound may decompose when in contact with air, light, moisture, heat, or storage and use above room temperature, releasing toxic, corrosive, flammable, or explosive gases. Thermal decomposition products include oxides of carbon, sulfur, nitrogen, and acid halides. It is incompatible with alkaline and oxidizing materials (MSDS-OHS, 2001a).

2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate are stable at normal temperatures and pressure. Thermal decomposition products are oxides of carbon. Both compounds are incompatible with oxidizing materials, resulting in a fire or explosion. In addition, dust or air mixtures of 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) may ignite or explode. Explosion may also occur if 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate is exposed to heat (MSDS-OHS, 2001b,c).

The sensitizers for the positive photoresists are usually the derivatives of DNQ. DNQ sulfonates, which are soluble in organic solvents and insoluble in aqueous alkaline solutions, undergo a number of reactions on exposure to light, ultimately resulting in the formation of substituted indene carboxylic acid. This acid, unlike the starting DNQ, is readily soluble in aqueous alkaline solutions. The five-substituted derivatives of DNQ, found to be the best for preparing the positive photoresists, exhibit a strong absorption at the wavelengths of mercury emission lines of 365 nm and 405 nm and a lower absorption at 436 nm (Bednar et al., 1993).

2.3 Commercial Availability

<u>Sodium 1,2-naphthoquinonediazide-5-sulfonate</u>

Sodium 1,2-naphthoquinonediazide-5-sulfonate is supplied by ChemDesign Corporation (Fitchburg, MA) and MRI International (Newton, NJ) (Chemcyclopedia Online, 2004). Diazo chemistry is a specialty of ChemDesign Corporation, a member of the Bayer custom services group; chemicals are produced in 1000- to 4000-gallon reactors (Bayer US, undated). The compound is also available in the United States from the following suppliers listed in the

CHEMCATS database: ChemPacific USA Sales Marketing and Research Center (Baltimore, MD) (bulk quantities); Fluka Chemical Corporation (Ronkonkoma, NY) (100- and 500-g quantities with a purity ≥97%); Pfaltz and Bauer, Inc. (Waterbury, CT) (50-g quantities with a purity of 98%); Monomer-Polymer and Dajack Laboratories, Inc. (Feasterville, PA); and TCI America (Portland, OR) (ChemPacific USA, 2001; Fluka Chem. Corp., 2001; Pfaltz and Bauer, Inc., 1999a; Monomer-Polymer and Dajack Laboratories, Inc., 1998; TCI America, 2000a). Under the 1998 and 2002 Inventory Update Rule (IUR), Specialty Chemical Products Corporation was listed as a company manufacturing or importing sodium 1,2-naphthoquinonediazide-5-sulfonate (U.S. EPA, 2004). It is also produced by Esprix Technologies (Sarasota, FL) as Diazo 10 (Esprix Technologies, 1998). PC Associates Inc. (Livingston, NJ) is a manufacturer and world-wide distributor of the salt (monohydrate) with 95% minimum purity (PC Associates Inc., 2001).

<u>1,2-Naphthoquinonediazide-5-sulfonyl chloride</u>
Pfaltz and Bauer, Inc. (Waterbury, CT) supplies 10-gram to 5-kilogram quantities of 2-diazo-1,2-naphthoquinone-5-sulfonyl chloride (Pfaltz and Bauer, Inc., 1999b). It is also available from ChemDesign Corporation (Fitchburg, MA), MRI International (Newton, NJ), and TCI America (Portland, OR) (Chemcyclopedia Online, 2004; TCI America, 2000b). Under the 1998 and 2002 IUR, ChemDesign Corporation and Arch Chemicals, Inc. were listed, respectively, as companies manufacturing or importing the compound (U.S. EPA, 2004).

<u>2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)</u>
No U.S. producers or suppliers were found.

<u>2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate</u>
Under the 1998 and 2002 IUR, ChemDesign Corporation and Arch Chemicals, Inc. were listed, respectively, as companies manufacturing or importing 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate (U.S. EPA, 2004). Diversitec Corporation (Fort Collins, CO), a manufacturer of chemicals used in graphic arts, can produce esters of 1,2-naphthoquinone-2-diazide-5-sulfonic acid with 2,3,4-trihydroxybenzophenone to the degree of substitution required by a customer (Diversitec Corporation, 1999).

3.0 Production Processes

The production of a 1,2-naphthoquinone-2-diazide or a sulfo-substituted compound thereof from a 2-diazo-1-naphthalene-sulfonic acid or a sulfo-substituted compound thereof can be obtained using an aqueous alkaline solution containing iodine, an aqueous alkaline solution containing iodine dissolved in an organic solvent, or an aqueous alkaline solution containing an oxidizing agent and iodine or an iodine compound. The method provides good yields and gives a photoresist component free of contaminants. Diazotization and treatment of 2-amino-1,5-naphthalene disulfonic acid mono-sodium salt with sodium hydroxide and iodine produced 88.1% of sodium 1,2-naphthoquinone-2-diazide-5-sulfonate (Iida et al., 1999).

The relative amounts of trihydroxybenzophenone isomers formed during esterification with 1,2-naphthoquinonediazide-5-sulfonyl chloride depend on solvent polarity, base, reactant concentration, and reaction time. The proportions of the esters in the mixtures resulting from different reaction conditions equilibrated in the presence of base and 2,3,4-trihydroxy-

benzophenone to give a common mixture (Zampini et al., 1996). Naphthoquinonediazide derivative photosensitive compounds for positive resists can be prepared by condensation of phenolic OH-containing compounds with 1,2-naphthoquinonediazide-5-sulfonyl chloride in organic solvents by using dibasic amines (Shimosaki et al., 2001).

4.0 Production and Import Volumes

Under the 1986, 1990, 1994, 1998, and 2002 Inventory Update Rule (IUR), an aggregate production volume ranging between 10,000 lb (4535.9 kg) and 500,000 lb (226,800 kg) was reported for sodium 1,2-naphthoquinone-2-diazide-5-sulfonate, 1,2-naphthoquinone-2-diazide-5-sulfonyl chloride, and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate. In 1986 and 1990, the same range was reported for 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) (U.S. EPA, 2004). Additionally, 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) was listed among the 262 non-high production volume (HPV) potentially persistent chemicals for which the Interagency Testing Committee (ITC) solicited voluntary submission of use and exposure data in its 45th report to the EPA Administrator (TSCA-ITC, undated).

5.0 Uses

The majority of positive DNQ/novolak-based photoresists use mixtures of various DNQ-esters and positional isomers as the photoactive compounds (PACs). The condensation reaction of DNQ sulfonyl chloride with the polyhydroxylated ballast group can be highly regioselective, producing mixtures strongly favoring either even- or odd-numbered isomers (e.g., from triesters to octaesters) (Pandya et al., 1994). The five-substituted derivatives of DNQ were found to be the best for preparing the positive photoresists (Bednar et al., 1993).

<u>Sodium 1,2-naphthoquinonediazide-5-sulfonate</u>

Sodium 1,2-naphthoquinonediazide-5-sulfonate is a component of a polymer film for use as a near-field write-once memory medium (Kawai et al., 2001). It is used in the manufacture of presensitized printing plates and in the photosensitive layer for the production of waterless lithographic printing plate master (Goto et al., 1997; Kizu et al., 1996).

<u>1,2-Naphthoquinonediazide-5-sulfonyl chloride</u>

1,2-Naphthoquinonediazide-5-sulfonyl chloride is manufactured for lithographic applications (Marks, 2001). Numerous Japanese patents exist for the compound. It is a component of radiation-sensitive resin compositions for positive-working resists, semiconductor device fabrication, and for the manufacture of electronic parts, providing improved dry etching resistance and high-resolution patterns (Akiyama et al., 2001; Fujita et al., 2001; Kawahata et al., 2000; Nunomura et al., 2001; Takahashi, 2000). The composition protects film for color filter or spacer associated with intermediate electric insulator film among thin film transistors (Takeuchi et al., 2000). It is used for photolithography for forming intermediate electric insulator film and microlens; the microlens shows improved heat and solvent resistance, transparency, adhesion to substrate, and storage stability (Nishimura et al., 2000). As a reactant in heat-resistant photoresist resin composition, it provides controlled composition viscosity (Tomikawa et al., 2001). When used for positive-working light-sensitive resin composition containing organosilicon compounds, it creates a heat-resistant polyimide (Sasaki et al., 2001). Additionally, the compound can be used as an explosive (UTA, undated).

2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)
Diazonaphthoquinonesulfonic esters [5610-94-6] are ≤5 weight percent in the products AZ(R) P4110 Photoresist and AZ(R) P4620 Photoresist available from Clariant Corporation (Somerville, NJ) (Clariant Corporation, 2000, 2001; Hoechst Celanese, 1989b, 1994a). It is also found in the following photoresists supplied by Clariant: AZ 1915, AZ 5214, AZ EXP PLP 100XT, AZ P4210, AZ P4400, AZ P4620, and AZ(R) EXP P4903 (Georgia Tech Microelectronics Research Center, undated). [Note: In 1997, the specialty chemicals business of Hoechst AG merged with Clariant AG of Switzerland (Hoechst AG, undated).]

2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate
2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate is an ingredient in the following photoresists produced by Hoechst Celanese Corporation (Somerville, NJ): AZ 1350J-SF, AZ 1350B-SF, and AZ 1370-SF (Hoechst Celanese, 1989a, 1994b,c). [Note: The CASRN for 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate, which may be considered generic for any of seven isomers, may be a better choice than 5610-94-6 for the esters designated in the photoresist compositions listed in Georgia Tech Microelectronics Research Center (undated).]

6.0 Environmental Occurrence and Persistence

Total organic carbon from raw industrial wastewater from large-scale integrated circuit photoresist processing, containing 1,2-naphthoquinone-2-diazido-5-sulfonic acid sodium salt as a main component with high sodium chloride concentration (>20 kg/m^3 [>2%]), was removed by treatment with hydrogen peroxide and ultraviolet (UV) irradiation, resulting in complete mineralization of the organic compounds (Hou et al., 2001). The use of chlorine or sodium hypochlorite and hydrogen peroxide in a second step was found to successfully treat wastewaters containing the salt (Iida et al., 2001). In the wastewater from a Japanese plant producing negative photoresist material, anaerobic digestion using microbes separated from soils and sludges decomposed >98% of 1,2-naphthoquinone-2-diazido-5-sulfonic acid sodium salt within four days, but degraded only 10% of the derivatives formed by oxidation and photochemical decomposition within 24 days (Hirata et al., 2000).

7.0 Human Exposure

Exposure to the DNQ derivatives may occur during the manufacture and use of products containing the compounds, particularly photolithography processes in the microelectronics industry. No specific information regarding workplace exposures to the DNQ derivatives was available.

8.0 Regulatory Status

The four DNQ derivatives in this report are listed on the Toxic Substances Control Act (TSCA) Inventory.

Sodium 1,2-naphthoquinonediazide-5-sulfonate, at a concentration of 100%, is on the list of self-reactive materials authorized for transportation and not subject to the approval provisions in Section 173.124(a)(2)(iii) (49 CFR 173.224) (DOT, 1998). Under the dangerous goods

regulation of the International Maritime Organization, the compound is not accepted in self-reactive solid type D substances (UN No. 3226) (IMO, undated).

Under the Superfund Amendments and Reauthorization Act (SARA) Title III Sections 311-312 (40 CFR 370.21), 1,2-naphthoquinonediazide-5-sulfonyl chloride is not an acute or chronic health hazard, and no sudden releases are expected. It is, however, a flammable and reactive hazard. The substance is also subject to disposal regulations (40 CFR 262 [Hazardous Waste Numbers: D001, D003]) and transportation regulations (40 CFR 172.101 [proper shipping name: Self-reactive solid type B; UN No. 3222]) (MSDS-OHS, 2001a).

Under SARA Title III Sections 311-312 (40 CFR 370.21), 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate are not hazards in the following categories: acute or chronic health, fire, reactive, and sudden release (MSDS-OHS, 2001b,c). Under the International Maritime Dangerous Goods (IMDG) code, both compounds have a UN number of 3226 (IMO, 2001).

9.0 Toxicological Data

9.1 General Toxicology

9.1.1 Human Data

Acute or short-term exposure to 1,2-naphthoquinonediazide-5-sulfonyl chloride may be irritating to the skin and the eyes (MSDS-OHS, 2001a).

9.1.2 Chemical Disposition, Metabolism, and Toxicokinetics

No data were available.

9.1.3 Acute Exposure

Acute toxicity values for 1,2-naphthoquinonediazide-5-sulfonyl chloride are presented in the table below.

Table 1. Acute Toxicity Values for 1,2-Naphthoquinonediazide-5-sulfonyl Chloride

Route	Species (sex and strain)	LD_{50}	Reference(s)
oral	mouse (sex and strain n.p.)	>3200 mg/kg (11.91 mmol/kg)	Eastman Kodak Co. (1992)
	rat (sex and strain n.p.)		
i.p.	mouse (sex and strain n.p.)	200 mg/kg (0.744 mmol/kg)	
	rat (sex and strain n.p.)	400 mg/kg (1.49 mmol/kg)	

Abbreviations: i.p. = intraperitoneal(ly); LD_{50} = lethal dose for 50% of test animals; n.p. = not provided

When rats and mice received an i.p. administration of the LD_{50} values for 1,2-naphthoquinonediazide-5-sulfonyl chloride, deaths occurred between four hours and three days. Surviving rats had rough coats, while surviving mice (except for two animals) had normal weight gain. When applied to the eyes of rabbits, the compound (100 mg; 0.372 mmol) caused slight to moderate irritation (i.e., erythema); two weeks later, all eyes were normal. When held in contact with the depilated skin of guinea pigs for 24 hours, 1,2-naphthoquinonediazide-5-sulfonyl

chloride (0.25, 0.50, or 1.0 mg/kg [0.93, 1.9, 3.7 µmol/kg] body weight) produced slight edema and staining. After one week, desquamation and staining were observed. After two weeks, only staining was still present (Eastman Kodak Co., 1992).

9.1.4 Short-term and Subchronic Exposure

1,2-Naphthoquinonediazide-5-sulfonyl chloride, incorporated (50% w/v) into a mixture of alcohol:glycerine (1:9 v/v) and applied to the clipped backs of guinea pigs at a rate of 0.5 mL/pig/day for ten days produced moderate to strong erythema associated with slight to moderate edema and numerous raised eschars (Eastman Kodak Co., 1992).

Male Charles River CD, COBS outbred rats fed 1,2-naphthoquinonediazide-5-sulfonyl chloride (0.1% or 1.0% w/w [up to 1000 mg/kg/day]) for 11 days had increased weight gain (109 and 103 g, respectively, for test animals versus 94 g for controls), mean hemoglobin concentrations, hematocrit, white blood cells, as well as slightly elevated serum levels of glutamic oxalacetic transaminase, lactic dehydrogenase, alkaline phosphatase, and urea nitrogen. The mean relative liver weights of the test animals were slightly lower than controls (12.09% and 11.88% for the 0.1% and 1.0% groups versus 12.66% for controls) (Eastman Kodak Co., 1992).

9.1.5 Chronic Exposure

No data were available.

9.1.6 Synergistic/Antagonistic Effects

No data were available.

9.1.7 Cytotoxicity

No data were available.

9.2 Reproductive and Teratological Effects

No data were available.

9.3 Carcinogenicity

No data were available.

9.4 Initiation/Promotion Studies

No data were available.

9.5 Anticarcinogenicity

No data were available.

9.6 Genotoxicity

No data were available.

9.7 Cogenotoxicity

No data were available.

9.8 Antigenotoxicity

No data were available.

9.9 Immunotoxicity

1,2-Naphthoquinonediazide-5-sulfonyl chloride was a potent skin sensitizer in guinea pigs. The animals were sensitized with injection of a compound-heparinized-whole-rabbit-blood reaction product into the footpads; subsequent challenge was by topical application of a solution of the compound (Eastman Kodak Co., 1992). No other data (e.g., dose) were provided.

9.10 Other Data

No other data were available.

10.0 Structure-Activity Relationships

Many other DNQ derivatives were identified, most of apparent little commercial importance. (See **Table 2** in Appendix B.) A gavage LD_{50} value of 8125 mg/L was reported for 1,2-naphthoquinonediazide-5-sulfonic acid [4857-48-1] in rats (Andrianov, 1987). Using the MultiCASE expert system to predict estrogen receptor binding capacity of a series of compounds, 1-diazonaphthoquinone-4-sulfonic acid [4857-47-0 or 887-76-3] was found to be inactive. Its relative binding activity (RBA) value was <0.001; the probability of the prediction being correct was 56% (Klopman and Chakravarti, 2003). No toxicity data were available for any of the other compounds.

11.0 Online Databases and Secondary References

11.1 Online Databases

Chemical Information System Files

TSCATS (Toxic Substances Control Act Test Submissions)

DIALOG Files

DIOGENES (DIOGENES®—Institution of Electrical Engineers)

STN International Files

AGRICOLA	CHEMCATS	NIOSHTIC
BIOSIS	EMBASE	NTIS
BIOTECHNO	ESBIOBASE	Registry
CA	IPA	RTECS
CABA	LIFESCI	TOXCENTER
CANCERLET	MEDLINE	TOXLINE
CAPLUS	MSDS-OHS	TOXLIT

TOXCENTER includes toxicology data from the following files:

Aneuploidy	ANEUPL*
BIOSIS Previews® (1969-present)	BIOSIS*
CAplus (1907-present)	CAplus
International Labour Office	CIS*
Toxicology Research Projects	CRISP*
Development and Reproductive Toxicology	DART®*

Environmental Mutagen Information Center File	EMIC*
Epidemiology Information System	EPIDEM*
Environmental Teratology Information Center File	ETIC*
Federal Research in Progress	FEDRIP*
Health Aspects of Pesticides Abstract Bulletin	HAPAB
Hazardous Materials Technical Center	HMTC*
International Pharmaceutical Abstracts (1970-present)	IPA*
MEDLINE (1951-present)	MEDLINE
Pesticides Abstracts	PESTAB*
Poisonous Plants Bibliography	PPBIB*
Swedish National Chemicals Inspectorate	RISKLINE
Toxic Substances Control Act Test Submissions	TSCATS*

*These are also in TOXLINE. Missing are TOXBIB, NIOSHTIC®, NTIS.

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No secondary reference sources were used.

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Appendix A: Units and Abbreviations

°C = degrees Celsius
DNQ = diazonaphthoquinone
DOT = Department of Transportation
g = gram(s)
IMO = International Maritime Organization
i.p. = intraperitoneal(ly)
IUR = Inventory Update Rule
kg = kilogram(s)
L = liter(s)
LD_{50} = lethal dose for 50% of test animals
mg/kg = milligram(s) per kilogram
mmol = millimole(s)
mmol/kg = millimoles per kilogram
mol = mole(s)
mol. wt. = molecular weight
NIEHS = National Institute of Environmental Health Sciences
nm = nanometer(s)
n.p. = not provided
SARA = Superfund Amendments and Reauthorization Act
TSCA = Toxic Substances Control Act

Appendix B: Description of Search Strategy and Results

Description Of The Strategy Used To Identify Diazonapthoquinonesulfonate Esters Used In Photoresists And Their Precursors And Relevant Chemical Information

Identification

A Registry file search August 27, 2001, linking name fragments naphthalenesulfonic, diazo, and ester retrieved 2,559 compounds, of which 21 were listed under TSCA. Seventeen compounds were retrieved using the name fragment diazonaphthoquinon? Two were in the set of 21 and six others were included in the table: L398a, L398c, L399a-21, L399a-22 (a TSCA-listed ester that did not conform to the strategy that retrieved the other 21 TSCA compounds), L399b-01, and L399b-03. In January 2002, the retrieval of CAPLUS records and MSDSs indicated that other commercial diazonaphthoquinonesulfonates might be identified. Generally, various permutations of the 9CI names and other systematic names of the sulfonic acids, sodium salts, or diazonium forms were tried in the Registry index of complete names with the use of the expand command followed by examination of nearby names. The names of several phenols mentioned in reviews as phenolic ballast compounds were expanded to identify specific diazonaphthoquinonesulfonate ester derivatives (variations recognized from the nomenclature used for the esters already compiled). Unfortunately, no uniform use of simple names was found in the trade literature. When simple names were found, they were usually ambiguous. In the table, I have usually selected only one or two other names besides the 9CI name. I sometimes provided names not in the Registry record but that were analogous to other names in the series.

Internet searches in January 2002 to find manufacturers' product data on the sulfonic acids, their diazonium counterparts, the sulfonyl chlorides, and photoresist compositions helped to identify other commercial compounds and confirmed commercial use of some of the TSCA-listed esters.

Toxicity

Systematic chemical name fragments were used in the August 2001 simultaneous search of MEDLINE, CANCERLIT, TOXLINE, AGRICOLA, NIOSHTIC, BIOTECHNO, EMBASE, CABA, BIOSIS, ESBIOBASE, and LIFESCI. No relevant records were retrieved by this approach. Use of several apparent trade names such as PAC (photoactive compound) I, PAC II, PAC III, and NT 200 and use of acronyms DNQ, NDQ, DAQ, DQN, and DQS found several records, but these reduced to fewer than 20 when combined with "diazo? OR photo? OR cresol? OR phenol? OR novola?" None of these records included relevant toxicity information. Some studies were on photodynamic treatment of tumor cells, diffusion in cell walls of plant roots, and proton transfer in bacterial cells. Most of the 22 records resulting from use of diazo? combined with resist? were about the patterning of proteins or neuronal and glia cells on photoresists. [These results overlapped slightly with those from the February 3, 2001, search for "diazonaphthoquinone OR 53208-22-3 OR naphthalenone within two words of diazo OR naphthoquinone diazide" (two records from TOXLINE, one from EMBASE, and three from BIOSIS).] In January 2002, additional combinations of name fragments were tried in the free PubMed and TOXLINE files with no success.

A final recheck of all of the TSCA compounds for test submissions on January 15, 2002, found no additional studies. Additional search terms used in RTECS besides the CASRNs were diazoquinonesulfon? OR diazoquinonesulphon? (zero records) and naphthalenesulfon? or naphthalenesulphon? (120 records) combined with diazo. The latter terms retrieved only the test submission by Eastman Kodak on sulfonyl chloride L398a. [A sulfonyl chloride is a reactive acylating agent and would be expected to be more irritating and more biologically reactive than the sulfonic acids, their salts, or their ester derivatives.]

None of the material safety data sheets found in MSDS-OHS and on the Internet during the earlier package preparation and during the supplemental compilation in January 2002 contained toxicity information other than comments about irritancy.

Other Topics

Registry records for additional compounds did not indicate that their CASRNs had been used to index any of them in the biomedical files. The Registry records of nine compounds indicated that CIN, PROMT, TOXLIT, and TOXCENTER database records were available. Eight new records resulted from searches of these databases. Ten compounds had suppliers identified in the CHEMCATS (chemical catalogs) database; eight of these had at least one U.S. supplier.

On January 15, 2002, a search was conducted in the sections of CAPLUS that cover environmental pollution and industrial hygiene for all of the CASRNs in the table of compounds. This was another approach to identify additional compounds as commercial products or as byproducts of industrial processes. The few results are discussed in the notes to the table. This was the only systematic search of CAPLUS. Other CAPLUS records were sometimes retrieved with the Registry record, which in the ALL format gives up to 10 of the most recent records at a low cost. Evidence was found that the ester precursors (L397 and L398 compounds) may also be used during device fabrication, not just during manufacture of the esters or photoresists.

Results

Information about the nearly 50 compounds identified has been summarized in a table as requested on 22 October 2001. The 17-page table (Table 2 in this Appendix) includes the following:

- The Ninth Collective Index (9CI) systematic chemical name
- Simpler names and trade names [No truly simple non-trade names were used by more than a few sources.]
- Listing in the TSCA inventory (or failing that, listing in the EINECS inventory)
- Listing in the U.S. EPA TSCA Inventory Update Rule data (only one firm each for three compounds)
- Other evidence for commercial production and use
- Evidence for environmental release
- Availability of toxicity and other physiological information
- Listing of databases searched and numbers of records per compound
- Molecular structures (which necessitated placing some of the comments in footnotes)

Diazonaphthoquinonesulfonic Acids and Derivatives Search Update

Search Strategy

Databases and Date Searched: Files MEDLINE, CANCERLIT, AGRICOLA, NIOSHTIC, BIOTECHNO, EMBASE, ESBIOBASE, CABA, IPA, BIOSIS, TOXCENTER, LIFESCI, and NTIS were searched simultaneously on August 30, 2004, with the CAS RNs and name fragments of all of the compounds in Table 2 of the draft. In the search session history below, the CAS RNs that returned zero results were omitted. Results were reduced to those published in the years 2002-2004 since the last search was done in January 2002. Two of the three (answer set L59) were relevant to the report.

In addition, a search of the Inventory Update Rule database for all CAS RNs found only information for

- 3770-97-6 (6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonyl chloride (production data and a producer: Arch Chemicals, Inc.);
- 2657-00-3 (6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonic acid sodium salt) (a producer: Special Chem Products Corp.); and
- 68510-93-0 (2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate) (producer: Arch Chemicals, Inc.).

These are three of the four compounds in the draft report. The range given for production of 3770-97-6, 10,000 to 500,000 pounds, is the same throughout the period 1986-2002.

Search Session History and Database Tallies:

```
L1            4 S 20546-03-6
L3            2 S 2657-00-3
L4            2 S 20680-48-2
L6            1 S 64173-96-2
L8            1 S 4857-47-0
L9            2 S 20541-54-2
L10           1 S 124529-10-8
L11           6 S 3770-97-6
L12           2 S 36451-09-9
L16           1 S 31600-99-4
L27           1 S 124364-82-5
L28           5 S 5610-94-6
L29           4 S 68510-93-0
L33           1 S 32060-64-3
L37           9 S 68584-99-6
L38           1 S 123759-89-7
L41           5 S 107761-81-9
```

```
L51          30 S L1 OR L3 OR L4 OR L6 OR L8-L12 OR L16 OR L27-L29 OR
                L33 OR L37 OR L38 OR L41
                SAVE L51 DNQCASRNS/A
L52           6 S DIAZO(6A)(SULFON? OR SULPHON?)(6A)(NAPHTHOQUINONE OR
                NAPHTHALENESULFON? OR NAPHTHALENESULPHON? OR NAPHTHOL OR
                DIHYDRONAPHTHALENE OR NAPHTHALENONE OR OXONAPHTHALENE)
L53          14 S DIAZIDE(6A)NAPHTHOQUINONE(6A)(SULFON? OR SULPHON?)
L54           0 S DIAZONAPHTHOQUINONESULFON? OR DIAZONAPHTHOQUINONESULPHON?
L55          16 S (DIAZONAPHTHOL OR NAPHTHOQUINONEDIAZIDE OR
                NAPHTHALENEDIAZONIUM)(6A)(SULFO? OR SULPHO?)
L56          35 S L52 OR L53 OR L55
L57          56 S L51 OR L56
L58           3 S L57 AND (2002-2004)/PY
                SET DUPORDER FILE
L59           3 DUP REM L58 (0 DUPLICATES REMOVED)
                ANSWER '1' FROM FILE BIOSIS
                ANSWERS '2-3' FROM FILE TOXCENTER
L60          53 S L57 NOT L58
L61          52 DUP REM L60 (1 DUPLICATE REMOVED)
              1 ANSWER '1' FROM FILE MEDLINE
              2 ANSWERS '2-3' FROM FILE EMBASE
              1 ANSWER '4' FROM FILE IPA
              2 ANSWERS '5-6' FROM FILE BIOSIS
             46 ANSWERS '7-52' FROM FILE TOXCENTER
L62           6 SORT L61 1-6 TI
L63          52 SORT L61 1-52 TI
                SAVE L63 DNQRNFRAG/A
L64           5 S DIAZONAPHTHOQUINONE
L65           4 S L64 NOT L57
L66           4 DUP REM L65 (0 DUPLICATES REMOVED)
              1 ANSWER '1' FROM FILE EMBASE
              1 ANSWER '2' FROM FILE ESBIOBASE
              2 ANSWERS '3-4' FROM FILE TOXCENTER
L67           0 S L66 AND (2002-2004)/PY
```

One of the search results was on the diazonaphthol dye sulfazo III. Additional abstracts on sulfazo III were subsequently retrieved from the same databases and are described. One abstract and the Registry record are included here.

Search Results:

Environmental Occurrence, etc.:

Han et al. (2002) reported on the occurrence and treatment of 1-diazo-2-naphthol-4-sulfonic acid in industrial wastewater.

Acute Toxicity:

A rat oral LD_{50} for 1,2-naphthoquinonediazide-5-sulfonic acid was determined to be 8125 mg/L (Andrianov, 1987).

Structure-Activity Relationships:

Klopman and Chakravarti (2003) used the MultiCASE expert system to predict estrogen binding capacity of a series of compounds including 1-diazonaphthoquinone-4-sulfonic acid. Bouchet et al. (1987) used 8-sulfonato-1-naphthalenediazonium chloride (20653-35-6) as an irreversible probe for the GABA receptor in rat brains. This compound was not in Table 2 of the original

draft; it is missing an oxo group. One PubMed search record shows 4-Diazo-3-hydroxy-1-naphthalenesulfonic acids were shown to be thrombopoietin (TPO) mimics during screening for the induction of a luciferase reporter gene in a TPO-responsive cell line (Duffy et al., 2001).

Mason et al. (1978) concluded that "futile formation of the sulfonazo III anion free radical mediates oxygen reduction to O_2^- and NADPH oxidation." *Results Not in This File*: Mason and coworkers have published several studies on the metabolism of sulfonazo III (orthanilic S). For example, Mason et al. (1977) reported that microsomal azo reduction of sulfonazo III produced an azo free radical anion metabolite. Stoddart and Levine (1992; PMID 1599508) used a cytosolic fraction of the rabbit liver to study azo reduction of sulfonazo III by aldehyde oxidase. Sulfonazo III is a compound that can produce a pro-oxidant state *in v*ivo (Knobeloch et al., 1990; PMID 2110585). Studies of TNF-alpha inhibition and TNA-alpha receptor binding by polysulfonated suramin structural analogs included sulfonazo III (Mancini et al., 1999; PMID 10449196). Yao et al. (1999) also studied interactions of sulfonazo III with proteins.

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists

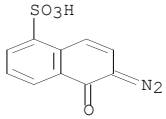
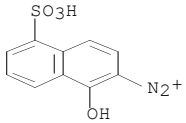
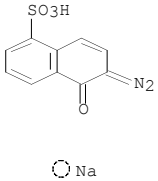
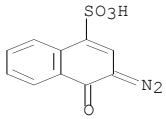
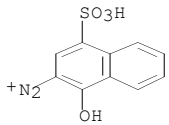
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
2-Diazo-1,2-naphthoquinone-5-sulfonic acid; 1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo- (9CI); 2,1,5-Diazonaphthoquinonesulfonic acid **[See Note L397a.]** **Commercial Use: DT, E**	20546-03-6	L397a	No	195	CHEMCATS (1; 0 USA) 
2-Diazo-1-naphthol-5-sulfonic acid; 2-Naphthalenediazonium, 1-hydroxy-5-sulfo- (9CI) **Commercial Use: T**	23890-27-9	L397a+	Yes/ No	7 (01/11/02)	
Sodium 1,2-naphthoquinone-2-diazide-5-sulfonate; 1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, sodium salt (9CI); Sodium 2,1-diazonaphthol-5-sulfonate **[See Note L397a · Na]** **Commercial Use: M, P, S, T, W**	2657-00-3	L397a · Na	Yes/ Yes	46 (01/14/02)	CHEMCATS(8; 5 USA), TOXCENTER (2), TOXLIT (1) 
2-Diazo-1,2-naphthoquinone-4-sulfonic acid; 1-Naphthalenesulfonic acid, 3-diazo-3,4-dihydro-4-oxo- (9CI); 1,2-Naphthoquinone-2-diazide-4-sulfonic acid; 2,1,4-Diazonaphthoquinonesulfonic acid **[See Note L397b.]** **Commercial Use: DT, E, S**	20680-48-2	L397b	No	81	CHEMCATS (3; 1 USA), TOXLIT (1) 
2-Diazo-1-naphthol-4-sulfonic acid; 2-Naphthalenediazonium, 1-hydroxy-4-sulfo- (9CI)	16926-71-9	L397b+	No	3 (01/11/02)	

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

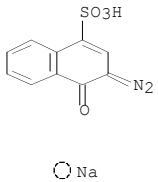
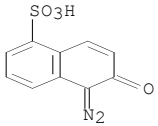
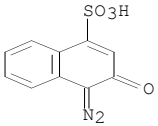
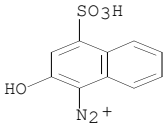
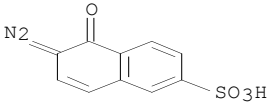
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1,2-Naphthoquinone-2-diazide-4-sulfonic acid, sodium salt (9CI); Sodium 1,2-naphthoquinone-2-diazide-4-sulfonate **[See Note L397b · Na]** **Commercial Use: P, S, T**	64173-96-2	L397b · Na	Yes/No	14 (01/14/02)	CHEMCATS (5; 3 USA), CIN (1), TOXCENTER (1), TOXLIT (1) 
1-Diazo-1,2-naphthoquinone-5-sulfonic acid; 1-Naphthalenesulfonic acid, 5-diazo-5,6-dihydro-6-oxo- (9CI)	4857-48-1	L397c	No	7 (01/08/02)	
1-Diazo-1,2-naphthoquinone-4-sulfonic acid; 1-Naphthalenesulfonic acid, 4-diazo-3,4-dihydro-3-oxo- (9CI); 2,1-Naphthoquinone-1-diazide-4-sulfonic acid **[See Note L397d.]** **Commercial Use: P, S**	4857-47-0	L397d	No	22 (01/10/02)	CHEMCATS (1 USA), TOXLIT (1) 
1-Diazo-2-naphthol-4-sulfonic acid; 1-Naphthalenediazonium, 2-hydroxy-4-sulfo- (9CI) **[See Note L397d+.]** **Commercial Use: P, S, T**	20541-54-2	L397d+	Yes/ No	24 (01/10/02)	
2-Diazo-1,2-naphthoquinone-6-sulfonic acid; 2-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo- (9CI) **[See Note L397e.]** **Commercial Use: P, W**	124529-10-8	L397e	No	4 (01/15/02)	TOXCENTER (1), TOXLIT (1) 

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

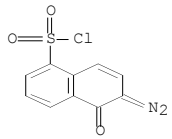
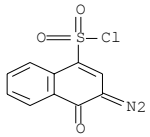
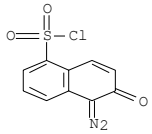
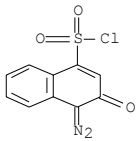
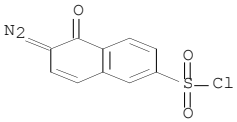
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
2-Diazo-1,2-naphthoquinone-5-sulfonyl chloride; 1-Naphthalenesulfonyl chloride, 6-diazo-5,6-dihydro-5-oxo- (9CI) **[See Note L398a.]** **Commercial Use: DT, S**	3770-97-6	L398a	Yes/ Yes	526	CHEMCATS (5; 3 USA), MSDS-OHS, RTECS, TOXLINE (1), TSCATS (1) 
2-Diazo-1,2-naphthoquinone-4-sulfonyl chloride; 1-Naphthalenesulfonyl chloride, 3-diazo-3,4-dihydro-4-oxo- (9CI) **[See Note L398b.]** **Commercial Use: DT, M, S**	36451-09-9	L398b	Yes/ No	301	CHEMCATS (4; 1 USA), MSDS-OHS 
1-Diazo-1,2-naphthoquinone-5-sulfonyl chloride; 1-Naphthalenesulfonyl chloride, 5-diazo-5,6-dihydro-6-oxo- (9CI)	20584-13-8	L398c	No	8	
1-Diazo-1,2-naphthoquinone-4-sulfonyl chloride; 1-Naphthalenesulfonyl chloride, 4-diazo-3,4-dihydro-3-oxo (9CI) **[See Note L398d.]** **Commercial Use: P**	38626-82-3	L398d	No	4 (01/10/02)	
1-Diazo-1,2-naphthoquinone-6-sulfonyl chloride; 2-Naphthalenesulfonyl chloride, 6-diazo-5,6-dihydro-5-oxo- (9CI) **[See Note L398e.]** **Commercial Use: P**	103452-31-9	L398e	No	9 (01/15/02)	

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

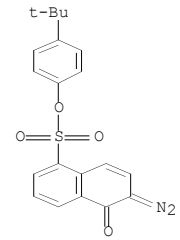
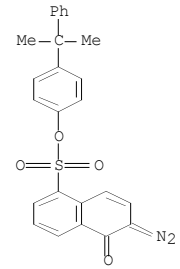
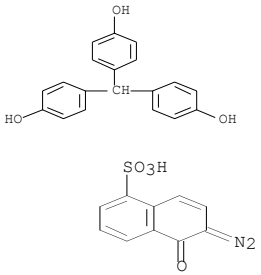
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
4-*tert*-Butylphenyl 2-diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonate; 1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo- 4-(1,1-dimethylethyl)phenyl ester (9CI); PAC I **Commercial Use: T**	31600-99-4	L399a-01	Yes/ No	47	MSDS-OHS 
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-(1-methy-l-phenylethyl)phenyl ester (9CI); PAC II **Commercial Use: T**	71728-47-7	L399a-02	Yes/ No	20	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with 4,4′,4′′-methylidynetris[phenol] (9CI); Tris(4-hydroxyphenyl)methane 1,2-naphthoquinonediazide-5-sulfonic acid ester **Commercial Use: T**	138636-86-9	L399a-03	Yes/ No	35	

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

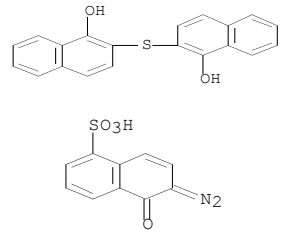
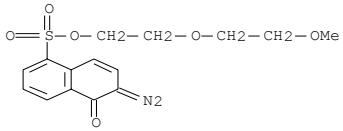
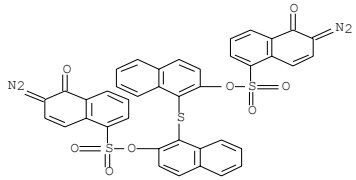
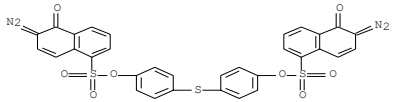
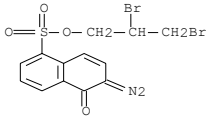
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with 2,2´-thiobis[1-naphthalenol] (9CI) [unspecified degree of esterification] **Commercial Use: T**	118276-85-0	L399a-04	Yes/ No	0	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 2-(2-methoxyethyl)ethyl ester (9CI) **Commercial Use: T**	71550-36-2	L399a-05	Yes/ No	0	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, thiodi-1,2-naphthalenediyl ester (9CI) **Commercial Use: T**	68901-25-7	L399a-06	Yes/ No	1	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, thiodi-4,1-phenylene ester (9CI) **Commercial Use: T**	68901-24-6	L399a-07	Yes/ No	0	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 2,3-dibromopropyl ester (9CI) **Commercial Use: T**	42372-37-2	L399a-08	Yes/ No	3	

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

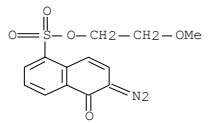
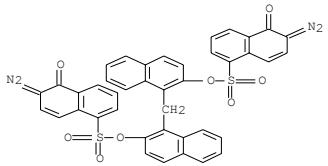
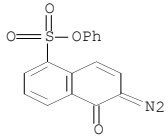
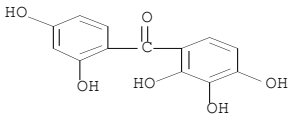
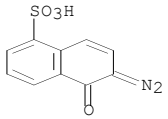
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 2-methoxyethyl ester (9CI) **Commercial Use: T**	42372-33-8	L399a-09	Yes/ No	5	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, methylenedi-1,2-naphthalenediyl ester (9CI); 1,1´-Methylenedi-2-naphthol bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) **Commercial Use: T**	33910-44-0	L399a-10	Yes/ No	26	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, phenyl ester (9CI); Phenyl 1,2-naphthoquinone-2-diazido-5-sulfonate **Commercial Use: T**	23295-00-3	L399a-11	Yes/ No	53	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with(2,4-dihydroxyphenyl) (2,3,4-trihydroxyphenyl)methanone (9CI); 2,2´,3,4,4´-Pentahydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate [unspecified degree of esterification] **Commercial Use: T**	124364-82-5	L399a-12	Yes/ No	15	 

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

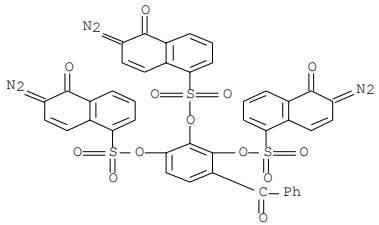
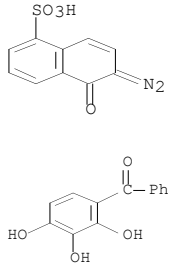
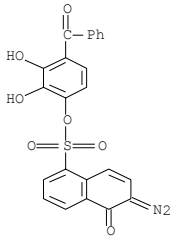
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-benzoyl-1,2,3-benzenetriyl ester (9CI); 2,3,4-Trihydroxybenzophenone tris(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate); Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate); NT 300; PAC III **[See Note L399a-13.]** **Commercial Use: M, MS, S, T**	5610-94-6	L399a-13 [formerly L399a]	Yes/ Yes	223	MSDS-OHS 
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with phenyl (2,3,4-trihydroxyphenyl) methanone (9CI); 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate; 2,3,4-Trihydroxybenzophenone 2,1,5-diazonaphthoquinonesulfonate [unspecified degree of esterification]; NQD; NT 200; THBP 215 **[See Note L399a-14.]** **Commercial Use: M, MS, S, T**	68510-93-0	L399a-14 [formerly L399b]	Yes/ Yes	158	MSDS-OHS 
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-benzoyl-2,3-dihydroxyphenyl ester (9CI); 2,3,4-Trihydroxybenzophenone 4-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) **Commercial Use: T**	2481-86-9	L399a-15	Yes/ No	33	

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

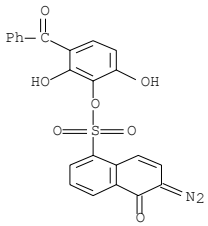
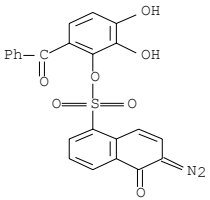
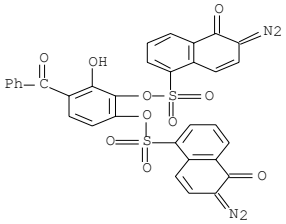
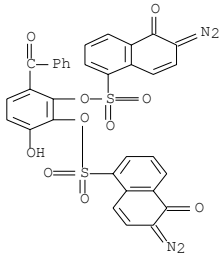
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 3-benzoyl-2,6-dihydroxyphenyl ester (9CI); 2,3,4-Trihydroxybenzophenone 3-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) **Commercial Use: T**	75578-78-8	L399a-16	Yes/ No	4	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 6-benzoyl-2,3-dihydroxyphenyl ester (9CI); 2,3,4-Trihydroxybenzophenone 2-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) **Commercial Use: T**	75578-79-9	L399a-17	Yes/ No	6	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-benzoyl-3-hydroxy-1,2-phenylene ester (9CI); 2,3,4-Trihydroxybenzophenone 3,4-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) **Commercial Use: T**	32060-64-3	L399a-18	Yes/ No	26	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 3-benzoyl-6-hydroxy-1,2-phenylene ester (9CI); 2,3,4-Trihydroxybenzophenone 2,3-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) **Commercial Use: T**	75578-77-7	L399a-19	Yes/ No	5	

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

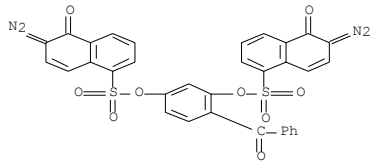
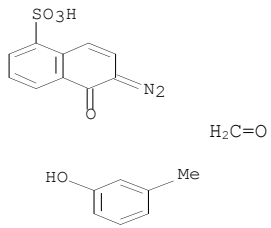
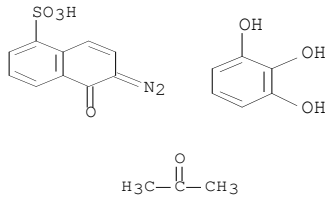
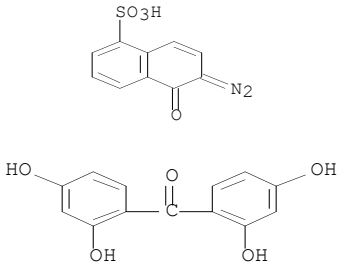
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-benzoyl-1,3-phenylene ester (9CI); 2,4-Dihydroxybenzophenone bis(1,2-naphthoquinone-2-diazide-5-sulfonate) **[See Note L399a-20.]** **Commercial Use: M, T**	31001-73-7	L399a-20	Yes/ No	64	CHEMCATS (4; 0 USA) 
Formaldehyde polymer with 3-methylphenol, 6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate (9CI); *m*-Cresol-formaldehyde copolymer 1,2-diazonaphthoquinone-5-sulfonate **Commercial Use: T**	62655-78-1	L399a-21	Yes/ No	88	
Acetone-pyrogallol copolymer 1,2-diazonaphthoquinone-5-sulfonate; 2-Propanone, polymer with 1,2,3-benzenetriol, 6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate (9CI); P 3000 **[See Note L399a-22.]** **Commercial Use: S, T**	68584-99-6	L399a-22	Yes/ No	375	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with bis(2,4-dihydroxyphenyl)methanone (9CI); 2,2′,4,4′-Tetrahydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate **[See Note L399a-23.]** **Commercial Use: P**	123759-89-7	L399a-23	No	6 (01/10/02)	TOXCENTER (1) 

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

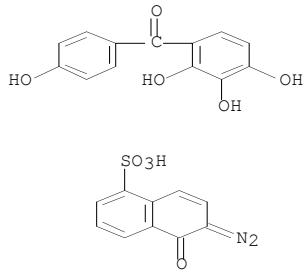
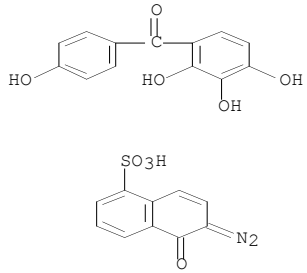
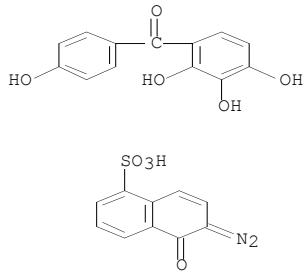
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, triester with (4-hydroxyphenyl) (2,3,4-trihydroxyphenyl) methanone (9CI); 2,3,4,4´-Tetrahydroxybenzophenone 1,2-naphthoquinone-2-diazido-5-sulfonic acid triester; 2,3,4,4´-Tetrahydroxybenzophenone 1,2-naphthoquinone-2-diazido-5-sulfonyl chloride ester (3:1) [unspecified attachments]	105935-62-4	L399a-24	No	47 (01/11/02)	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, diester with (4-hydroxyphenyl) (2,3,4-trihydroxyphenyl) methanone (9CI); 2,3,4,4´-Tetrahydroxybenzophenone bis(1,2-naphthoquinonediazido-5-sulfonate); 2,3,4,4´-Tetrahydroxybenzophenone ester with naphthoquinone-2-diazide-5-sulfonic acid (1:3) [unspecified attachments]	114571-69-6	L399a-25	No	12 (01/11/02)	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with (4-hydroxyphenyl) (2,3,4-trihydroxyphenyl) methanone (9CI); 2,3,4,4´-Tetrahydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate [unspecified ratio; unspecified attachments]	107761-81-9	L399a-26	No	228 (01/11/02)	MSDS-OHS 

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

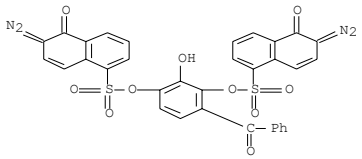
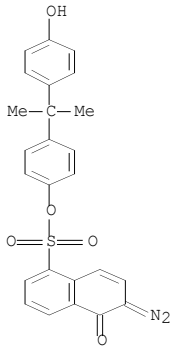
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-benzoyl-2-hydroxy-1,3-phenylene ester (9CI); 2,3,4-Trihydroxybenzophenone 2,4-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) **[See Note L399a-27.]** **Commercial Use: E, P**	93965-14-1	L399a-27	No	4 (01/15/02)	
1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-[1-(4-hydroxyphenyl)-1-methylethyl)phenyl ester (9CI); Bisphenol A monoester of 2-diazonaphthoquinone-5-sulfonic acid; 1,2-Naphthoquinonediazide-5-sulfonic acid 2,2-bis(hydroxyphenyl)propane monoester **[See Note L399a-28.]** **Commercial Use: P**	53155-39-8	L399a-28	No	18 (01/17/02)	CHEMCATS 
1-Naphthalenesulfonic acid, 3-diazo-3,4-dihydro-4-oxo-, 4-benzoyl-1,2,3-benzenetriyl ester (9CI); 2,3,4-Tris(1-oxo-2-diazonaphthoquinone-4-sulfonyloxy)benzophenone; D 4SB; NT (4)300; NT Ester-4-sulfonic acid **[See Note L399b-01.]** **Commercial Use: E**	84522-08-7	L399b-01	No	68	Structural analog of L399a-13 in which the sulfonyl group is attached to C-4 instead of C-5.

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

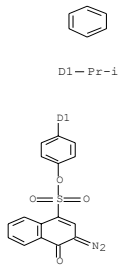
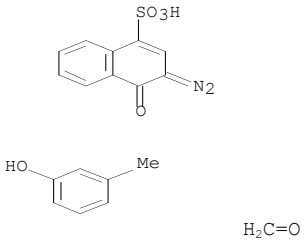
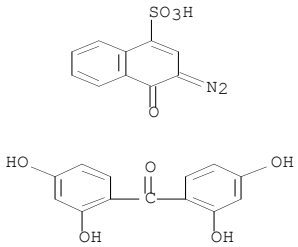
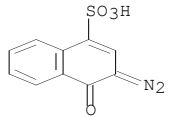
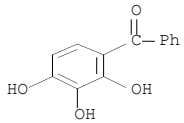
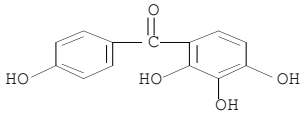
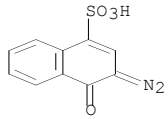
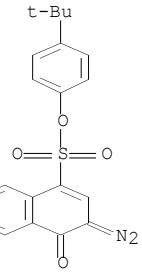
Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 3-diazo-3,4-dihydro-4-oxo-, ar´-(1-methylethyl)[1,1´-biphenyl]-4-yl ester (9CA); *p*-Cumylphenyl-1,2-naphthoquinone-2-diazide-4-sulfonate **Commercial Use: MS, S, T**	52125-43-6	L399b-02	Yes/ No	8	CHEMCATS (1 USA), MSDS-OHS, TOXCENTER (5) 
Formaldehyde polymer with 3-methylphenol, 3-diazo-3,4-dihydro-4-oxo-1-naphthalenesulfonate (9CI); *m*-Cresol-formaldehyde copolymer 1,2-naphthoquinonediazide-4-sulfonate	129290-81-9	L399b-03	No	12	
1-Naphthalenesulfonic acid, 3-diazo-3,4-dihydro-4-oxo-, ester with bis(2,4-dihydroxyphenyl)methanone (9CI); 2,2´,4,4´-Tetrahydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonic acid ester **Commercial Use: P**	132176-10-4	L399b-04	No	4 (01/10/02)	

Table 2. Results of Literature Search to Identify Report-Relevant Information on Diazonaphthoquinonesulfonic Acid Derivatives Used Commercially in Photoresists (Continued)

Chemical Name and Evidence for Commercial Use [See First Key to Codes]	CASRN	ILS Code	TSCA/ EPA IUR	CA Records 08/27/01	Relevant Databases (No. of Records) and Structure
1-Naphthalenesulfonic acid, 3-diazo-3,4-dihydro-4-oxo-, ester with phenyl (2,3,4-trihydroxyphenyl) methanone (9CI); 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinone-2-diazide-4-sulfonic acid ester	125857-81-0	L399b-05	No	22 (01/11/02)	 
1-Naphthalenesulfonic acid, 3-diazo-3,4-dihydro-4-oxo-, ester with (4-hydroxyphenyl) (2,3,4-trihydroxyphenyl) methanone (9CI); 2,3,4,4´-Tetrahydroxybenzophenone 1,2-naphthoquinonediazide-4-sulfonate [unspecified ratio; unspecified attachments]	124760-77-6	L399b-06	No	27 (01/11/02)	 
4-tert-Butylphenyl 1,2-naphthoquinone-2-diazide-4-sulfonate; 1-Naphthalenesulfonic acid, 3-diazo-3,4-dihydro-4-oxo- 4-(1,1-dimethylethyl)phenyl ester (9CI); 4-*tert*-Butylphenyl 2-diazo-1-oxo-1,2-dihydronaphthalene-4-sulfonate **[See Note L399b-07.] Commercial Use: P**	58886-62-7	L399b-07	No	8 (01/15/02)	

Key to Codes for Evidence for Commercial Use:

- DT indicates that TSCA-listed derivatives may be produced from this compound.
- E indicates that the compound is listed under EINECS (European Inventory of Existing Commercial Chemical Substances).
- M indicates that one or more U.S. producers (Manufacturers) have been identified.
- MS indicates that Material Safety Data Sheets (MSDSs) are available.
- P indicates that some support is available in patents as described in the individual compound notes.
- S indicates that one or more U.S. suppliers, other than producers have been identified.
- T indicates that the compound is regulated under the Toxic Substances Control Act (TSCA).
- W indicates that the compound is found in waste.

Key to ILS Compound Codes:

L397 compounds are sulfonic acids. L398 compounds are sulfonyl chlorides. L399 compounds are sulfonic acid esters (sulfonates).

The a suffix indicates a 1-naphthalenesulfonic acid or derivative with 6-diazo, 5-oxo, and 5,6-dihydro substituents.

The b suffix indicates a 1-naphthalenesulfonic acid or derivative with 3-diazo, 4-oxo, and 3,4-dihydro substituents.

The c suffix indicates a 1-naphthalenesulfonic acid or derivative with 5-diazo, 6-oxo, and 5,6-dihydro substituents.

The d suffix indicates a 1-naphthalenesulfonic acid or derivative with 4-diazo, 3-oxo, and 3,4-dihydro substituents.

The e suffix indicates a 2-naphthalenesulfonic acid or derivative with 6-diazo, 5-oxo, and 5,6-dihydro substituents.

The plus sign has been appended to the letter suffix of the corresponding diazonium analog.

General Notes:

Comprehensiveness of Compounds Identified: The basic search strategy was to examine only the TSCA-listed compounds resulting from a Registry file search statement "1(with)naphthalenesulfonic(with)acid(linked to)diazo(linked to)ester." The Ninth Collective Index (9CI) name has generally conformed to these name fragments in most of the diazonaphthoquinonesulfonic acid esters found by other strategies based on their mention in commercial photoresist compositions or the supposition that they might exist based on technical literature lists of phenolic compounds used in production of the esters. Examples of commercial or TSCA-listed esters of L397a-L397d+ (or L398a-d) were not found for all of the polyhydroxybisphenylalkanes mentioned in the state-of-the-art recapitulated by Kawata et al. (1992). No attempt was made to identify and include esters of the 2-naphthalenesulfonic acid L397e or its sulfonyl chloride (L398e), which were included in the table late in its compilation.

Evidence for Commercial Use: Listing under TSCA and availability of an MSDS in the MSDS-OHS database are noted in the table. Other evidence mentioned in the footnotes that support commercial use includes presence in photoresist compositions with MSDSs available on the Internet, listing in EINECS, and mention in patents. However, the patent literature was not retrieved and examined for L397b+, L397c, L398c, L399a-24, L399a-25, and L399b-03 through

L399b-06, compounds for which no other evidence of commercial use was found. Checks of the business databases PROMT and CIN (Chemical Industry Notes) found one relevant record, a premanufacturing notice (PMN) for L397b. The three PROMT records were not noted in the table because they were incorrectly indexed for L399a-01 [presumably an automated selection based on a character string that matched a synonym (PAC I)]. U.S. suppliers were sought in the CHEMCATS (Chemical Catalogs) database. Notes on quantities sold, if available, as well as the supplier name(s) are included in the notes on the individual compounds.

Physiological Data: Certain name fragments were used to search the biomedical databases (see fuller description in attached search strategy description), but as the list grew, reliance on absence of physiological information was based on the absence of biomedical database listings in the Registry record. That listing is based solely on the use of the CASRN in the database. The physiological data for L397d+ was found among the 10 most recent CAPLUS records supplied for a low additional fee with the Registry record in the ALL format. Except for some notations that the compounds are irritants, no toxicity information was found in the MSDS-OHS records for L398a, L398b, L399a-01, L399a-26, and L399b-02. TOXCENTER and TOXLIT records with physiological information had generally surfaced from other sources. In the TOXCENTER records (all originally from CAPLUS), some Japanese patent abstracts stated that the novel photoresist composition were nontoxic or of low toxicity. The probable reason was apparently the switch in solvents from those based on ethylene glycol to ones based on propylene glycol. The basis for inclusion of other records was not obvious.

Regulations: Compounds listed under TSCA are indicated in the table. If producers of 10,000 lb or more of any of these compounds are included in the U.S. EPA Inventory Update Rule (EPA IUR) database, these have been noted in the table and the producers named in the appropriate footnote. Several of these compounds are mentioned specifically or generally in transport regulations. L398a and L398b are considered to be self-reactive materials. Their esters (not identified individually) and the sodium sulfonates are also listed as self-reactive with UN No. 3226. DOT Emergency Response Guide 149 applies to these materials.

Note L397a: Although not in the TSCA inventory, L397a is on the EINECS list.

Note L397a · Na: Suppliers: The EPA IUR database (U.S. EPA, 2000) lists Specialty Chemical Products Corporation as a U.S. producer of L397a · Na. The salt is also available in the United States from Chemetall Chemicals Products, Inc. (Chemcyclopedia 2002), Esprix Technologies (1998), PC Associates Inc. (2001), and the five suppliers in the CHEMCATS database: ChemPacific USA Sales Marketing and Research Center (ChemPacific USA, 2001) (bulk quantities), Fluka Chemical Corporation (2001) (100- and 500-g quantities), Pfaltz and Bauer (1999) (50 g), Monomer-Polymer and Dajack Laboratories, Inc. (1998), and TCI America (2000). ChemDesign Corporation produces the compound, offering it as "diazo-2,1,5-sulfonic acid, sodium salt." ChemDesign Corporation "provides custom manufacturing services for fine organic chemicals plants" and "is a part of Bayer Organic Chemicals business." Diazo chemistry is one of its specialties. Chemicals are produced in 1,000- to 4000-gal reactors (Bayer US, undated). [In these Notes, when the supplier named is the primary source of the information, the date of the supplier's publication (catalog entry as given by CHEMCATS or product data from the company's web site) has been appended directly to the supplier name. These records are filed by company name in the references used in the preparation of this table.]

Uses: The ten most recent CAPLUS records indicate in the patents (no U.S. companies) that the salt may be used for lithographic plate printing as well as a photoresist in microelectronics fabrication.

Environmental Releases: The sodium salt is "a main component" in photoresist processing waste waters from large-scale integrated circuit manufacture and is difficultly treatable in the presence of the high sodium chloride concentrations (> 20 kg/m^3 [>2 %]). Treatment with hydrogen peroxide and ultraviolet irradiation gave complete mineralization of the organic compounds (Hou et al., 2001). Iida et al. (2001) found that use of chlorine or sodium hypochlorite and hydrogen peroxide in a second step successfully treated wastewaters containing L397a · Na. Hirata et al. (2000) found the salt in the wastewater from a Japanese

plant producing negative photoresist material. Activated microbial degradation decomposed >98% within 4 days, but degraded only 10% of the derivatives formed by oxidation and photochemical decomposition within 24 days.

Note L397b: Although not in the TSCA inventory, L397b is on the EINECS list. Fluka Chemical Corporation (2001) supplies it in 50- and 250-g quantities.

Note L397b · Na: The salt is available from PC Associates Inc. (2001). U.S. EPA (1990) published notice of receipt of a PMN for L397b · Na from Specialty Chemical Products Corporation (The CIN record was indexed for L397b, but the salt is named in the abstract.) The three suppliers in CHEMCATS were Davos Chemical Corporation (2000) (bulk quantities), Pfaltz and Bauer, Inc. (1999) (10 and 100 g), and TCI America (2000). The salt is mentioned in a few Japanese patents as a photosensitizer for lithographic plates, dental polymers, and photoresists. Blumel and Deutsch (1986) in a patent assigned to Fairmount Chemical Co., Inc., USA, used this salt in a coating for a photoresist layer on an oxidized silicon wafer to enhance image contrast. **In this example, the sodium salt was used directly during microelectronics device fabrication.** A Japanese patent for a composite adhesive resin for bonding dental filling materials to dentin or enamel included L397b · Na in the composition for initiating photopolymerization (Sato et al., 1998), a direct, if minor, human exposure.

Note L397d: Only three CAPLUS records for L397d contained the term "photoresist?" The first was a patent assigned to Fujitsu Ltd., Japan, and the other two were patents assigned to UCB S.A., Belgium. Bulk quantities are available from ChemPacific USA (2001). Milligram quantities are available from Scientific Exchange, Inc. (2001). No TSCA-listed esters were identified by expanding the 9CI name in the Registry file. None of the esters identified had more than one CAPLUS record, so they were not added to the table. The 7-nitro derivative (63589-25-3) was listed under TSCA and had 20 CAPLUS records as of 08 January 2002. Since nitro-substituted esters were not found in the photoresist trade literature, no further searches were done. Klopman and Chakravarti (2003) used the MultiCASE expert system to predict estrogen binding capacity of a series of compounds including L397d.

Note L397d+: Kessler Chemicals Inc. (1999) sells L397d+ in amounts of at least 500 kg (≥227 lb). This diazonium compound is used in dye synthesis (based on 5 of the 10 most recent CAPLUS records). Han et al. (2002) [Chinese article] reported on the occurrence and treatment of L397d+ in industrial water. Duffy et al. (2001) of GlaxoSmithKline and Luengo et al. (2000) reported that the compound, among several other hydroxyazonaphthalene and hydrazinonaphthalene compounds, is a thrombopoietin mimic and may be useful in the treatment of thrombocytopenia. Bayer Corporation USA (Pugia and Schaeper, 1997; Noffsinger et al., 1996) was assigned patents for the use of L397d+ for determination of leukocyte elastase in urine. Duc et al. (1999) reported that cells of *Rheum palmatum* (rhubarb) metabolized L397d+ without releasing the metabolites, which indicated potential for decontamination of industrial effluents.

Note L397e: This sulfonic acid or its salts may be found in organic wastewaters from synthesis of derivatives according to a Japanese patent (Iida et al., 2001). Aoso and Kokubo (1997) of Fuji Photo Film Co., Ltd., Japan, produced a photoresist composition containing an ester of L397e, and Roland et al. (1989) of UCB S.A., Belgium, mentioned photoresists with diazoquinone derivatives prepared from L397a-e and L397b.

Note L398a: Suppliers: A.H. Marks and Co. Ltd. (Marks, 2001) (United Kingdom) manufactures L398a, L398b, and their esters as the principal compounds among the "several tens of tonnes of products" produced annually. The EPA IUR database lists ChemDesign Corporation as a U.S. producer. L398a is listed on the web site as "diazo-2,1,5-chloride," a name that appears to be used by only ChemDesign and Bayer (Bayer US, undated). Suppliers in the CHEMCATS database were TCI America (2000) and Pfaltz and Bauer, Inc. (1999). The latter supplies L398a in amounts up to 5.0 kg; the 1999 price for that amount was about $135/lb.

Toxicology: The TOXLINE and TSCATS records for L398a were for a TSCA test submission by Eastman Kodak Company. Besides the usual acute oral toxicity (mice and rats) and eye and dermal irritation studies in rabbits and guinea pigs, the studies included dermal sensitization in guinea pigs and two

"subchronic" studies. The results of the short-term studies and the 10-day (intermittent) dermal exposure subchronic study in guinea pigs are in RTECS. The rat dietary study is not in the RTECS record.

Note L398b: ChemDesign Corporation, a Bayer custom services group, produces this compound, offering it under the name "diazo-2,1,4-chloride" (Bayer US, undated). Davos Chemical Corporation (2000) is a bulk supplier.

Note L398d: Three of the four patents in CAPLUS were about preparation of the sulfonyl chloride. The CAPLUS record for a patent assigned to Hoechst Celanese Corporation, USA (Khanna and Ptwin, 1992), described use of sulfonyl chlorides with 2,3,4,4´-tetrahydroxybenzophenone to prepare a photosensitizer for positive photoresists. The CASRNs for L398c and L398d are in the indexing, but L398a and L398b are the reactants mentioned in the abstract. [This would not be unusual so long as the CASRNs for L398a and L398b were in the indexing, too. The abstract generally describes only one of many examples from a chemical patent.]

Note L398e: Among the nine CAPLUS records are several patents by Japanese companies, including Sumitomo Bakelite Co., Ltd., Sumitomo Chemical Co., Ltd., and Clariant Japan.

Note L399a-13: L399a-13 was among 262 non-HPV potentially persistent chemicals for which ITC had no use and exposure data. The deadline for submission of such data was 15 April 2000 (TSCA-ITC, undated). http://tsca-itc.syrres.com/Chemicals/Pub/262.pdf. Clariant Corporation photoresist compositions that contain L399a-13 include AZ 5214, AZ EXP PLP 100XT, AZ P4110, AZ P4210, AZ P4400, AZ P4620, AZ(R) EXP P4903, and AZ 1915 (Georgia Tech Microelectronics Research Center, undated http://grover.mirc.gatech.edu/data/chem_main/index.phtml?type=photoresist; Clariant Corporation, 2000, 2001). Thirteen MSDS-OHS records on 27 August 2001 showed compositions for formaldehyde-xylenol-cresol copolymer-based photoresists that contained L399a-13. No commercial affiliation is indicated in the MSDS-OHS records.

Note L399a-14: The CASRN for L399a-14 may be considered generic for any of seven isomers (L399a-13, L399a-15 to –19, L399a-27) and may be a better choice than 5610-94-6 for the esters designated in the photoresist compositions listed in Georgia Tech Microelectronics Research Center (undated). The relative amounts of the isomers formed during esterification with L398a depend on solvent polarity, base, reactant concentration, and reaction time. The proportions of the esters in the mixtures resulting from different reaction conditions equilibrated in the presence of base and 2,3,4-trihydroxybenzophenone to give a common mixture (Zampini et al., 1996). DiCarlo et al. (1994) reported on the analytical determination and characterization of the seven isomers. The CASRN for L399a-14 was listed as an ingredient by Hoechst-Celanese (1989, 1994a-c) in the photoresist compositions AZ 1350J, AZ 1350B-SF, and AZ 1370-SF. [Clariant was created when Clariant Ltd., near Basel, Switzerland, bought former Hoechst Celanese Corporation's specialty chemical division.] The only producer listed in the EPA IUR database (U.S. EPA, 2000) is ChemDesign Corporation. Diversitec Corporation (1999) will produce esters of L397a with 2,3,4-trihydroxybenzophenone to the degree of substitution required by the customer. The MSDS-OHS record for pure L399a-14 contained no toxicity information. Seven other MSDS records retrieved on 27 August 2001 were on photoresist formulations containing L399a-14, most of which were based on formaldehyde-cresol copolymers.

Note L399a-20: Diversitec Corporation (1999), a manufacturer of chemicals used in graphic arts in Fort Collins, CO, will produce esters of 2,4-dihydroxybenzene with L397a to customers' specifications on degree of substitution.

Note L399a-22: Such an ester based on L397a+ is MIPHOTO PAC-200 from a Korean company (Miwon Commercial Co., Ltd., undated).

Note L399a-23: The six CAPLUS records were for patents for photoresist compositions containing this ester. The patents were assigned to Japanese companies including Sumitomo Chemical Co., Mitsubishi, Fuji Photo Film Co., and Toshiba. Diversitec Corporation (1999) will produce esters of L397a with unspecified isomers of tetrahydroxybenzophenone to the customers' desired degree of substitution. Products are used in graphic arts.

Note L399a-27: Although not in the TSCA inventory, the compound is in EINECS. A Japanese patent described its use in a photoresist.

Note L399a-28: This bisphenol A ester is available from Secant Chemicals Inc. (undated) as the "Monoester of 2-Diazo-1-naphthol-5-sulfonic acid with Bisphenol A." According to the ten most recent CAPLUS records, the ester is used in photoresists as well as in films for cartography and lithographic printing plates. The only U.S. users may be Kodak Polychrome Graphics (Sheriff and Schneebeli, 1999) and Eastman Kodak USA (West et al., 1998) (patents for lithographic plate photosensitive compositions).

Note L399b-01: Although not in the TSCA inventory, the compound is in EINECS and the Canadian Domestic Substances List.

Note L399b-02: The MSDS-OHS database has records for at least three photoresist compositions containing this ester. Davos Chemical Corporation (2000) is a bulk supplier.

Note L399b-04: The four CAPLUS records were for photoresist patents assigned to Japanese and Italian companies.

Note L399b-07: Four of the eight CAPLUS records were Japanese patents for photoresist compositions or lithographic plates.