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In 1993, U.S. Navy submarine crews began to notice yellowing of the bulkheads and other structures during underway periods and sea trials. The yellowing was reported to General Dynamics Electric Boat Division (EBD) as a failure of the paint system. EBD conducted a thorough investigation and found that the yellowing was not caused by failure of the paint coating system, but, instead, by 2,6-Di-tert-butyl-4-Nitrophenol (DBNP). DBNP is formed when lubricating oil mist containing 2,6-Di-tert-butylphenol (DBP), an antioxidant additive in many synthetic lubricating oils and hydraulic fluids, passes through an electrostatic precipitator, and is nitrated. DBNP is an intensely yellow crystalline material. Submarine personnel coming into contact with DBNP on bedding, bulkheads, or other surfaces noted yellowing of their skin and requested information from the medical department regarding the hazards of exposure. EBD's data indicated that although the yellowing was most pronounced in the engineering compartments, DBNP moves throughout the submarine in the ventilation system. This finding indicates that DBNP could reasonably be expected to accumulate on dishes, glasses, flatware, bedding, and other items leading to ingestion as well as dermal contact and inhalation as potential routes of exposure. Analysis of the EBD data indicated identifiable DBNP concentrations in the air at several locations in the submarine. Concentrations ranged from 3.0 to 13 ppb. EBD also conducted laboratory simulations of the submarine environments finding DBNP concentrations as high as 122 ppb. In 1961, Vesselinovitch et al. reported the LD 50 for DBNP as 500 mg/kg in Sprague-Dawley rats. (2) Holder et al., concentrating on the ingestion route of exposure, reported that DBNP was toxic in mammals and that approximately 30 percent of the oral dose was absorbed. (3) As a pilot study to determine the range of the LD 50 in rats, a new acute oral study was conducted by the Naval Health Research Center Toxicology Detachment (NHRC/TD), using Fischer 344 rats with corn oil as the vehicle. The intent of this study was to validate the findings, specifically to replicate the LD 50 , of the Vesslinovitch study. 2 Findings of the new study indicated the LD50 in rats at 80 mg/kg making DBNP significantly more toxic then previously recognized. 4 Differences in the findings were attributed to differences in rat strain and the

vehicle. In 1999, a second acute oral study, sponsored by NHRC/TD, was conducted in Sprague-Dawley rats to validate findings of the 1998 study and for further comparison to the 1961 study. Results of the second study supported the LD 50 at 80-100 mg/kg in rats. (5) While DBNP yellowing seemed to be confined to the closed environment of submarines during underway periods, anecdotal information was also received from petroleum manufacturers and suppliers that refineries were noting yellowing of the walls and equipment. Additionally, submarine services from other nations are now beginning to report yellowing aboard their submarines. There is little information on DBNP in the published literature. DBNP is a yellow crystalline powder with a melting point at 157oC and a molecular weight of 251. It is soluble in organic solvents, but relatively insoluble in water. Reviews of the literature indicated that very little was known regarding the toxicity of DBNP. This chemical was proposed as a commercially available miticide in the late 1950s. A 1961 study by Vesselinovitch et al. determined the LD 50 values for guinea pigs, mice, and rats in oral and intraperitonneal exposures. 2 In that study, they determined the oral LD 50 in Sprague-Dawley rats to be in the 400-500 mg/kg range. DBNP was indicated as relatively non-toxic to humans. The 1961 study was conducted in Sprague-Dawley rats using carboxymethylcellulose as the vehicle. Rats were exposed to an oral bolus (0.2 ml/20 g of body weight) at each concentration of DBNP. No specific discussion referencing the manner of death was provided. Conclusions indicated that DBNP dosages were cumulative with increased mortality among animals given daily doses as small as 1sol;25 of the LD 50 for an unspecified period of time, believed to be less than 14 days. No discussion of the potential for enterohepatic circulation was provided. Vesselinovitch et al. reported a gender difference in DBNP toxicity with the LD 50 in females being slightly higher than in the males. (2) In a 1970 study, Holder et al. reported on excretion of DBNP. 3 They concluded that Vesselinovitch et al. had shown that DBNP was highly toxic to mammals in the 1961 study. 2 They indicated a significant relationship between DBNP and 3,5-Di-tert-butyl-hydroxy toluene (BHT), another antioxidant additive in lubricating oils and hydraulic fluids. This study was conducted using a 20 mg oral dose of radio-labeled carbon fourteen (14 C) DBNP. They reported that DBNP was poorly absorbed from the gut with approximately 30percent of the oral

dose excreted unchanged. The absorbed DBNP was excreted as a glucuronide conjugate. No other metabolites were identified. They found that DBNP administered orally was excreted primarily through feces and urine with a small percentage in the bile. The findings were equivocal on enterohepatic circulation. In a 1997 technical report, the Naval Medical Research Institute's Toxicology Detachment (NMRI/TD) characterized the metabolism, distribution, and toxicity of DBNP. (6)

* Ferrous metallurgical industries
* Non-ferrous metallurgical industries
* Mining industries
* Ores/mineral processing industries
* Coal (including coke) industries
* Power generating industries
* Paper and pulp (including paper products) industries
* Fertilizer industries
* Cement (including cement asbestos products) industries
* Petroleum industries
* Petrochemicals industries
* Drugs and pharmaceuticals industries
* Fermentation industries
* Rubber (natural and synthetic) including rubber products industries
* Paints industries
* Leather tanning industries
* Electroplating industries
* Chemical industries
* Insecticides, Fungicides, Herbicides and other pesticide industries
* Synthetic resins and plastics industries
* Manmade fibres (cellulose and non-cellulose industries).

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