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World Headquarters
Middlebury, Connecticut 06749

June 12, 1984

Dr. Carol R. Stack
C.M.A.
2501 M Street, N.W.
Washington, D. C. 20037

Dear Dr. Stack:

After considerable deliberations I have decided to retire on August 31, so must regretfully resign from the vinyl chloride panel as of that date. I will always cherish the association with the members of this committee over the years. The hectic days of 1974 will stand out in my memory.

Please extend my best wishes to Maurie Johnson and members of the panel. I'll be interested in the epidemiological update.

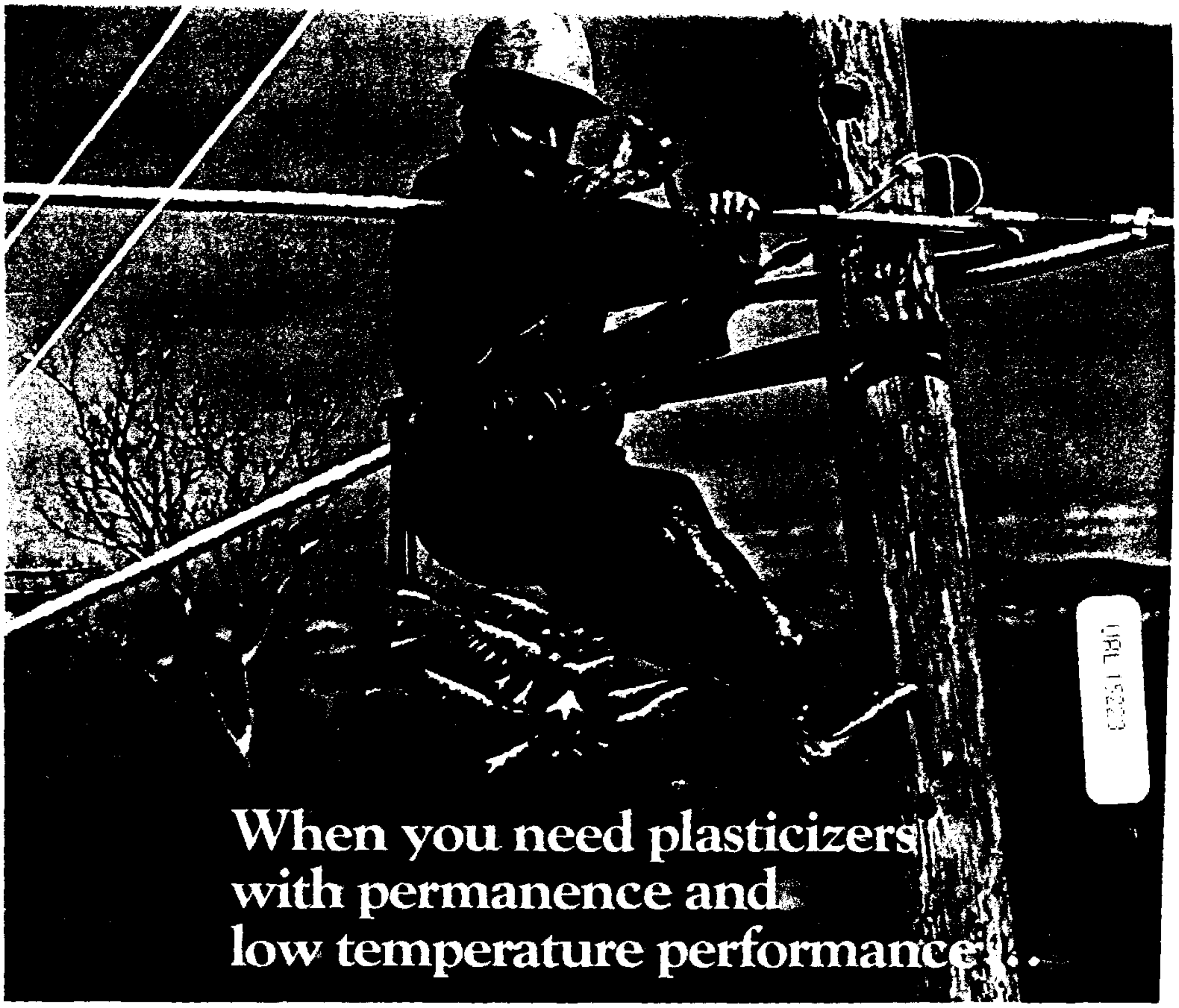
Sincerely,

Walter D. Harris

Walter D. Harris
Corporate Industrial Toxicologist

jm/
cc: J. D. ~~Foster~~ Forbes
[redacted]

URL 15222



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Vinyl chloride

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A history of polyvinyl chloride

1835. Justus von Liebig at the University of Giessen discovers that reaction of the "oil of the Dutch chemists" (ethylene dichloride) with alcoholic potash produces a chlorine-containing gas. Liebig assigns confirmation of the work to his student, Victor Regnault, and lets Regnault publish as sole author. As a result, Liebig is forgotten as the discoverer of vinyl chloride.

1872. E. Baumann finds that exposure of vinyl chloride to sunlight in a sealed tube produces a white solid that resists attack by potassium hydroxide or water and melts with decomposition above 130 °C.

1912. Chemische Fabrik Griesheim-Electron gives chemist Fritz Klatte the task of finding uses for acetylene, and he develops commercial synthesis of vinyl chloride by addition of hydrogen chloride.

1915. Klatte finds that organic peroxides initiate polymerization to polyvinyl chloride.

1926. After years of effort to develop rigid PVC as a replacement for celluloid, German workers have failed to build machinery that will process the resin and have not overcome the problem of thermal instability. Griesheim-Electron stops paying the fees that maintain its patents. Meanwhile in the U.S., Union Carbide, looking for uses for the ethylene dichloride by-product of chlorohydrin production, converts it to vinyl chloride with sodium hydroxide. PVC also interests Waldo L. Semon at B. F. Goodrich, who is looking for an adhesive to bond rubber to metal. Semon observes that boiling PVC in such liquids as tricresyl phosphate or dibutyl phthalate renders it highly elastic, thus discovering plasticizers. In addition to molding parts from plasticized PVC, Semon goes on to coat wire, cloth, and metal parts with solutions of PVC in plasticizer or plasticized PVC in organic solvents, thereby inventing plastisol and organosol processing techniques. He uses white lead and sodium silicate as heat stabilizers.

1928. Union Carbide and Du Pont each find that copolymers of vinyl chloride with vinyl acetate have improved processibility.

1934. Frazier Groff of Union Carbide discovers that alkaline earth soaps stabilize PVC to heat.

1936. Union Carbide's PVC homopolymer plant comes on stream at 4 million lb per year. Chemists there find that dialkyltin soaps are also heat stabilizers. At B. F. Goodrich, T. L. Gresham tests thousands of compounds before settling on di-2-ethylhexyl phthalate as the best plasticizer.

1941. During World War II, PVC is commandeered for military use, with the Navy in particular using large amounts of phosphate-plasticized, fire-retardant wire insulation developed by General Electric.

1947. One or more workers now unknown hit upon synergistic combinations of barium, cadmium, calcium, and zinc soaps as heat stabilizers.

1952. Elliott Weinberg at Metal & Thermit Corp. invents the dibutyltin dimercaptide with 2-ethylhexyl thioglycolate as a heat stabilizer for rigid PVC, and at the same time invents the antimony trimercaptide low-cost stabilizer for pipe, which will be commercialized 30 years later as tin prices skyrocket.

1960. U.S. production of PVC tops 1 billion lb.

1970. Pier Luigi Viola at Regina Elena Institute for Cancer Research in Rome finds that exposure to very high levels of vinyl chloride vapor causes ear tumors in rats. U.S. production of PVC tops 4 billion lb.

1973. Cesare Maltoni, working for a group of European firms at the Institute of Oncology in Bologna, Italy, finds that inhalation of vinyl chloride vapors causes rare angiosarcoma liver cancer in rats. The Manufacturing Chemists Association is allowed to see his work, but only under a confidentiality agreement. Forbidden to communicate Maltoni's findings, MCA commissions its own studies of rats and worker exposures. Late in the year, physician John L. Creech links deaths of two B. F. Goodrich workers from angiosarcoma to vinyl chloride exposure in Louisville, Ky. Eventually, angiosarcoma deaths of three dozen people worldwide are tied to vinyl chloride exposure.

1974. Goodrich tells the National Institute of Occupational Safety & Health of the cancer link. The Occupational Safety & Health Administration reduces permissible vinyl chloride exposure to 50 ppm from 500 ppm and proposes a "zero detectable limit." Industry spokesmen say that will force them to shut down. OSHA agrees to a phased reduction to 1 ppm. PVC makers announce that they can meet this and alter their plants to do so. Later, activists tar industry for saying first that the OSHA limit would shut them down and then agreeing that they can meet it.

1980. The National Cancer Institute finds evidence that di-2-ethylhexyl phthalate plasticizer causes cancer in rats and mice.

1982. Stung by inroads of PVC into pipe, metal-pipe makers counterattack with a campaign to warn public authorities of toxicity of gases emitted by PVC in fires.

1984. A recovering U.S. economy carries PVC use to a record 6.3 billion lb.

most used then are benzophenones and benzotriazoles. Also used are such acrylates as 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, which are also called acrylonitriles.

According to Joseph Stretanski, who is technical manager for plastics additives for American Cyanamid, benzophenones such as 2-hydroxy-4-methoxy- or 2-hydroxy-4-octoxybenzophenone usually are used in conjunction with barium-cadmium stabilizers, and such benzotriazoles as 2-(2-hydroxy-5-*tert*-octylphenyl)benzotriazole are used with tins. Benzophenones are yellow and contribute color to a clear vinyl compound. In applications such as a clear vinyl coating for a richly colored flooring tile, the slight yellowing may not matter. Benzotriazoles perform better than benzophenones and yield clear vinyl products that are water-white. So some