RECEIVED
OCT 22 1971

ACCEPTED
FEB 28 1972
UNDER THE FEDERAL INSECTICIDE, FUNGICIDE AND RODENT ACT AS FOR ECONOMIC POISON REGISTERED UNDER NO. 1258-688 SUBJECT TO ATTACHED COMMENTS

1258-688

ANTIDOTES

EXTERNAL

Flood with water for 15 minutes.

INTERNAL

Drink large quantities of water or milk. Follow with milk of magnesia, vegetable oil, or beaten eggs. Call Physician Immediately.

EYES

Wash eyes with water for 15 minutes. Get prompt medical attention.

MANUFACTURED FOR

Olin Corporation
120 Long Ridge Road
Stamford, Connecticut 06904

USDA Reg. No. 1258-688 CHG-871

CALCIUM HYPOCHLORITE
GRANULAR

For Manufacturing, Repacking, or Processing Use Only

ACTIVE INGREDIENT: Calcium Hypochlorite...........70%
INERT INGREDIENTS:.................................30%
AVAILABLE CHLORINE..............70%

DANGER - KEEP OUT OF REACH OF CHILDREN

MAY PRODUCE SEVERE CHEMICAL BURNS. DO NOT ALLOW CONTACT WITH EYES, SKIN, MUCOUS MEMBRANES, OR CLOTHING. HARMFUL OR FATAL IF SWALLOWED.

STRONG OXIDIZER
CONTACT WITH OTHER MATERIALS MAY CAUSE FIRE

KEEP FROM CONTACT WITH CLOTHING AND OTHER COMBUSTIBLE MATERIALS. DO NOT STORE NEAR COMBUSTIBLE MATERIALS. REMOVE AND WASH CONTAMINATED CLOTHING PROMPTLY.

Mix only with water. May cause fire if contaminated. Keep away from combustible organic material. Do not contaminate with any foreign matter. Contamination may result in fire and the fire will be of great intensity. Drench fire with water and cool the surrounding area with water. Prevent any burning materials such as a lighted cigarette from falling into container. Dispose of spilled product by flushing with large amounts of water. When transferring use only a clean, dry cup. Any foreign matter added to it may cause fire. A clean, dry container must always be used to carry this product to the pool. Do not mix with household products, acids, solvents or other pool chemicals. Keep in a cool, dry place. Always replace cover. Do not drop, roll or skid container. Keep upright. Do not re-use empty container. Wash empty container thoroughly with water and discard in a clean safe place.

See Antidote Statement on Reverse Side of Tag

HTH® DRY CHLORINE IN CYANIDE-WASTE TREATMENT

Many of the baths or solutions used in certain metal-treating operations require a cyanide component, usually added as sodium cyanide. These operations include electroplating, pickling and heat-treatment of steel, and the refining of gold and silver ores. They yield wastes in various volumes containing varying quantities of residual cyanides, depending on size and type of operation.

THE POLLUTION PROBLEM

All such wastes pose severe pollution problems, due to their cyanide (CN)− content. Toxicity of cyanides is very high. Discharged raw into sewers, streams or other watercourses or dumped on land, they can be dangerous. They are not only highly toxic to humans and animal life, but will also kill the bacteria upon which sewage-disposal plants depend for digestion of putrefactive material.

There is growing concern at all levels of government and among the general public about environmental pollution. There seems to be no doubt that controls aimed at reducing all forms of industrial pollution will become more and more stringent. Since cyanides are so toxic and so widely known to the public as poisons, regulations covering their discharge in wastes are already strict.

A typical regulation is that of the Indiana Stream Pollution Control Board, adopted in 1953. It reads, in part, as follows: "Any person, firm or corporation engaged in manufacture or other process in which cyanides or cyanogen compounds are used shall have each and every room, where said compounds are used or stored, so constructed that none of said components can escape therefrom by means of building sewer, drain or otherwise directly or indirectly into any sewer system or watercourse;

"Provided, however, that on application to and prior approval by the Stream Pollution Control Board, limited amounts, which it is determined would not be detrimental to public health or would not pollute any lake, river, stream, drainage or roadside ditch or other watercourse, shall not come under the provision of the paragraph above."

A check of similar regulations elsewhere indicates that the most stringent of them, limit the allowable concentration of cyanides to a level not greater than 0.1 ppm. Cyanide-users, both large and small, are faced with regulations such as these in disposing of their toxic wastes.

ALKALINE CHLORINATION

Alkaline chlorination is a widely used and very effective method of detoxification. It will reduce the cyanide level to 0.1 ppm. quite readily. It employs, in alkaline medium, either hypochlorites or gaseous chlorine (which forms hypochlorite ion in solution). Hypochlorite ion can oxidize cyanide to cyanate (CNO) and also break down the latter to carbon dioxide (CO_2) and nitrogen (N_2). The basic chemical reactions involved are shown below in abbreviated, ionic form:

$$Cl_2 + 2(OH) \rightarrow (Cl)^- + (OCl)^- + H_2O$$
$$(OCl)^- + (CN)^- \rightarrow (CNO)^- + (Cl)^-$$
$$2(CNO)^- + 3(OCl)^- + H_2O \rightarrow 2CO_2 + N_2 + 3(Cl)^- + 2(OH)^-$$

Usually, the quantity of cyanide wastes to be treated determines whether the gaseous-chlorine or the hypochlorite-compound route should be followed. The information contained herein pertains to operations that must dispose of small-to-moderate quantities of waste cyanide. These may also include larger processors who have, aside from their main waste streams, secondary sources of cyanide slops such as leaking equipment, overflows and floor drains. It is often preferable to accumulate such minor effluents and treat them sepaare considered to be those that generate less than 10,000 gallons of ordinary waste cyanide-containing solutions in an 8-hour period. This volume, in electroplating operations, would include both still- and running-rinses, "drag-outs" and necessary dumpings of spent baths. Operators needing to dispose of wastes in this range of volume will usually find it economical and convenient to use hypochlorite treatment.

ROLE OF HTH DRY CHLORINE

HTH dry chlorine manufactured by Olin is exceedingly well-suited to the needs of such operations. Chemically, it is calcium hypochlorite [$Ca(OCl)_2$] and contains approximately 70% available chlorine. Calcium hypochlorite is the most economical solid material suitable for alkali chlorination of cyanide wastes. This fact is important, because waste treatment is a non-productive, overhead expense. Good business practice dictates minimizing of controllable overheads. Being a stable, containerized solid, HTH dry chlorine is easy to store and use. It obviates any need for such auxiliary equipment as heavy, pressurized cylinders or treating-solution storage tanks. These factors help to minimize labor and equipment costs.

A SIMPLE TECHNIQUE: TWO "END-POINTS"

The way alkali chlorination of cyanide wastes works is as follows: There are two possible "end-points." The first represents oxidation of cyanides to relatively non-toxic and generally unobjectionable cyanates $(CNO)^-$. It is reached quickly (10-15 minutes) by moderate application of hypochlorite—theoretically about 2.7 parts of available chlorine per part of cyanide, (as CN). In this oxidation, pH is kept at about 10, to prevent the reaction from proceeding beyond the "cyanate end-point."

This reaction is slowed somewhat by the presence of monovalent nickel ions. Also, since oxidizable materials other than cyanides are usually present in cyanide wastes, the theoretical chlorine ratio may have to be increased by up to 25%. Ferrocyanides and ferricyanides contain the "CN" radical in a form not oxidizable by hypochlorites. However, small quantities of those complex cyanides are probably not serious pollutants in most cases. If necessary, they might be handled by aqueous dilution.

By using additional hypochlorite and lowering the pH to about 6.5, cyanates (free of cyanides) can be decomposed to nitrogen and carbon dioxide—the second and final "end-point". This reaction requires a theoretical dosage of available chlorine amounting to and nitrogen trichloride necessitate use of chlorine in quantities greater than theoretical. This reaction is relatively slow, requiring 1 to 1½ hours, or more, for completion.

If pH of approximately 8-8.5 is maintained throughout and adequate hypochlorite used, the decomposition can be carried out in a single stage, directly from cyanide to nitrogen and carbon dioxide.

TYPE OF TREATMENT INDICATED

Chemical treatment of cyanide wastes must usually be resorted to if it is impossible or unfeasible to dilute them to the generally acceptable discharge concentration of 0.1 ppm., or to hold them in lagoons for the slow, natural process of decomposition. Treatment with HTH dry chlorine can be done easily, using simple equipment, mainly a mixing tank. The theoretical quantity of HTH required to convert cyanides only to cyanates varies, somewhat, with composition of the liquor. The minimum requirement is approximately 4 pounds for each pound of cyanide, as CN. If monovalent copper and nickel are both present in solution, the requirement is approximately 4.7 to 5.5 pounds. Nickel present without copper necessitates using approximately 4.7 to 5.7 pounds.

Copper present without nickel requires somewhat less HTH—approximately 4.4 to 4.7 pounds for each pound of cyanide. (These bivalent metals consume some available chlorine in the process of oxidation to their higher valence states.) Probably in most cases, conversion of cyanides to cyanates will suffice to meet public disposal regulations.

OPERATING PROCEDURE—BATCH

Batch treatment is the commonest method of detoxifying cyanide wastes with solid hypochlorite, but continuous treatment can also be used. Tanks may be constructed of steel, concrete or wood, assuming that conditions which deteriorate these materials are avoided. They should be provided with an outlet for drainage and a clean-out port for sludge removal, and sized for maximum economy and convenience of operation. Pumps or stirrers are required for circulating and mixing the waste liquids and reagent.

The pH of waste liquor in the mixing tank should be checked before treatment and adjusted to 10 or slightly above, by means of sodium hydroxide (NaOH). The theoretical dosage of NaOH is approximately 1.13 pounds per pound of available chlorine being added. However, most cyanide wastes are alkaline to the extent of requiring only about 60 to 90% of theoretical caustic.

Mixing is necessary during pH adjustment. Caution: Care should always be taken, when handling cyanide wastes, to avoid letting the pH drop below 7.0, for fear of generating poisonous hydrogen cyanide gas.

Raw cyanide wastes should contain not more than 500 ppm. of cyanide before treatment. If original concentration exceeds 500 ppm., the waste must be diluted at least to that strength with water. This will avoid excessive rise in temperature from the heat of reaction. Temperature of the liquid before treatment should be lower than 120°F., preferably around 75°F. The requisite quantity of HTH granules should be added at a steady rate to the waste liquor in the mixing tank, with constant stirring. A recommended procedure is to broadcast the granules evenly over the surface, using a clean, dry, aluminum scoop. Note: Users of HTH Dry Chlorine are cautioned to read with care the instructions and precautionary information set forth on the labels affixed to the containers of the product.

TESTS AND CONTROLS

When the batch has been agitated for 15 minutes, a test with starch-iodide paper or other suitable reagent should be made for residual chlorine. If the test shows chlorine present, the treated batch should be held another hour without agitation to be doubly sure that no cyanide has escaped reaction. If another test made at the end of the hour still shows chlorine, and if it is determined to be 0.5 to 1.0 ppm., the waste may be considered free of cyanides. (Higher levels of chlorine can be diminished by addition of sodium sulfite or other antichlor material, if desired.)

Should the first test indicate absence of available chlorine, it is simply necessary to add more HTH with agitation. After 15 minutes of agitation, testing and holding as above should continue until adequate level of residual chlorine is reached and maintained. Treated waste liquor can usually be discharged directly to a sewer. Sludge that accumulates in tank bottoms is removed periodically and disposed of, typically by lagooning. If more-quantitative methods for determining cyanides are desired, they are to be found in a pamphlet published by the American Electroplating Society, Inc. It is entitled "The Analysis of Electroplating Solutions for Major Constituents."

During this operation, pH should be checked periodically. If necessary, additional NaOH should be added to maintain pH.

OPERATING PROCEDURES—CONTINUOUS

When either the use of the batch method is not practicable or continuous treatment is clearly preferable, cyanide wastes are usually accumulated in a basin or tank from which the treated discharge is metered continuously to sewers at a uniform concentration and rate. This is the basis for continuous treatment. The tank is for collecting purposes only. The actual reaction of cyanide and reagent takes place in the outflow line. Automatic controls for the feeding of sodium hydroxide and HTH dry chlorine solutions are provided along the effluent pipe line, allowing sufficient time-lapse and agitation for complete reaction along the route of flow. The solution of HTH dry chlorine can be obtained from hypochlorinator devices or by dissolving granules or tablets in water to make stock solution. Where necessary, provisions for diluting concentrated wastes must be provided. Careful laboratory control is advised in connection with the continuous process. to ensure that all effluent reaching the sewer is within the allowable local limits for residual cyanide.

COMPLETE DECOMPOSITION

When complete destruction of cyanides to nitrogen and carbon dioxide is required, the procedure is still essentially as described in the foregoing. The main differences, as previously mentioned, are that additional available chlorine, lower pH and greater reaction time are required. Only enough caustic soda to achieve a pH of 8.5 or slightly higher should be added to the raw waste cyanide liquor in the mixing tank, carefully avoiding acid conditions.

The theoretical minimum quantity of HTH dry chlorine required in this reaction is approximately 10.5 pounds for each pound of cyanide, as CN. When copper or nickel compounds, or both, are present, an additional 10 to 15% of HTH must be added as in the case of the simple oxidation to the cyanate stage. Stirring of the batch should continue for from one to two hours. Testing for residual chlorine to ensure completion of the reaction before dumping the treated waste should be carried out, the same as when cyanides are being converted to cyanates.

HTH AVAILABILITY

HTH dry chlorine is marketed as fast-dissolving granules and more slowly dissolving tablets. It is packaged in various polyethylene containers, 35 lb. capacity steel pails and 100 lb. capacity fiber drums.

TECHNICAL ASSISTANCE

In a generalized description of this sort, it is not possible to give detailed instructions suitable for every cyanide waste-treatment installation. Some may have special requirements in design, layout or other factors. The information contained herein can be supplemented, whenever required, by enquiries directed to your nearest Olin Chemicals sales office. Olin Technical Service is available to assist in such enquiries.

DISTRICT SALES OFFICES

Atlanta, Ga. 30309—1720 Peachtree St., N.W., (404) 875-8936
Charlotte, N. C. 28202—Baugh Bldg., (704) 333-1175
Cincinnati, O. 45237—8075 Reading Rd., (513) 761-7112
Hinsdale, Ill. 60521—120 E. Ogden Ave., (312) 325-2280
Houston, Tex. 77006—3015 Richmond Ave., (713) JA 6-2761
King of Prussia, Pa. 19406—210 Goddard Blvd., (215) 265-0900
New Orleans, La. 70130—1055 St. Charles Ave., (504) 529-5557
New York, N.Y. 10022—745 Fifth Ave., (212) 572-2924
Providence, R. I. 02903—Hospital Trust Bldg., (401) GA 1-2070
Shaker Heights, O. 44120—3570 Warrensville Ctr. Rd., (216) 752-0088
St. Louis, Mo. 63105—7710 Carondelet, (314) VO 3-5300
Whittier, Calif. 90602—13215 E. Penn Ave. (213) 945-1063

Olin CHEMICALS