OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETIC ACID

INTRODUCTION

This guideline summarizes pertinent information about acetic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_2H_4O_2$

- **Structure**

CH_3COOH

- **Synonyms**

Ethanoic acid, ethylic acid, glacial acetic acid, methanecarboxylic acid, vinegar acid

- **Identifiers**

1. CAS No.: 64-19-7

2. RTECS No.: AF1225000

3. DOT UN: 2789 29 (glacial acetic acid or acetic acid solutions that are more than 80% acid); DOT UN: 2790 60 (aqueous solutions that are more than 10% but not more than 80% acid)

4. DOT labels: Corrosive, Flammable Liquid (glacial acetic acid or acetic acid solutions that are more than 80% acid); Corrosive (aqueous solutions that are more than 10% but not more than 80% acid)

- **Appearance and odor**

At temperatures above 16.7°C (62°F), acetic acid is a clear, colorless, combustible liquid with a pungent, vinegarlike odor. The odor threshold is reported to be between 0.21 and 1.0 parts per million (ppm) parts of air. This substance is available commercially in strengths ranging from 6% to more than 99% acid, by weight. Glacial acetic acid is 99.4% acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data (glacial acetic acid)**

1. Molecular weight: 60.1

2. Boiling point (at 760 mm Hg): 118°C (244.4°F)

3. Specific gravity (water = 1): 1.05 at 20°C (68°F)

4. Vapor density (air = 1 at boiling point of acetic acid): 2.1

5. Melting point: 16.7°C (62°F)

6. Vapor pressure at 20°C (68°F): 11 mm Hg

7. Solubility: Miscible with water, alcohol, glycerol, carbon tetrachloride, and ether; insoluble in carbon disulfide

8. Evaporation rate (butyl acetate = 1): 1.0

- **Reactivity**

1. Conditions contributing to instability: Heat and freezing temperatures. The vapor of acetic acid forms explosive mixtures with air.

2. Incompatibilities: Fires or explosions may result from contact of acetic acid with chromic acid, ammonium nitrate, sodium peroxide, nitric acid, phosphorus trichloride, or other oxidizers.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released when acetic acid is heated to decomposition.

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4. Special precautions: Acetic acid is highly corrosive in concentrated form; it corrodes metals, some coatings, and some forms of plastic and rubber.

- **Flammability (glacial acetic acid)**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to glacial acetic acid.

1. Flash point: 39°C (103°F) (closed cup). The flash point of concentrated solutions of acetic acid approaches that of glacial acetic acid; dilute acetic acid solutions are not combustible.

2. Autoignition temperature: 427°C (800°F). Dilute acetic acid solutions are not combustible.

3. Flammable limits in air (% by volume): Lower, 4.0; upper, 16.0

4. Extinguishant: Use water spray, dry chemical, alcohol foam, or carbon dioxide to fight fires involving acetic acid. Use water spray to keep fire-exposed containers cool. If a leak or spill has not ignited, water may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving acetic acid should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetic acid. Firefighters' protective clothing may not provide protection against permeation by acetic acid.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetic acid is 10 ppm of air (25 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (25 mg/m^3) as an 8-hr TWA and 15 ppm (37 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetic acid a threshold limit value (TLV) of 10 ppm (25 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 15 ppm (37 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation to the eyes, nose, and respiratory tract associated with exposure to acetic acid.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetic acid can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: Glacial acetic acid is corrosive to tissues, and concentrated acetic acid solutions (greater than 80% acid) can cause moderate to severe burns. Exposure to the vapors of acetic acid causes eye, skin, mucous membrane, and upper respiratory tract irritation.

When applied to the skin of guinea pigs, acetic acid solutions of 80% or more caused severe burns; concentrations of 50% to 80% caused moderate to severe burns; concentrations of less than 50% caused relatively minor skin damage; and solutions of 10% or less caused no injury [Proctor et al. 1988]. When glacial acetic acid was applied to the eyes of rabbits, it caused immediate and complete destruction; splashes of less concentrated solutions caused less damage [Grant 1986]. The dermal LD_{50} for rabbits was 1,060 mg/kg [NIOSH 1991]. When acetic acid was inhaled, the lowest LC_{50} for mice and guinea pigs exposed for 1 hr was approximately 5,000 ppm [NLM 1991]. Guinea pigs exposed for 1 hr to airborne acetic acid concentrations ranging from 5 to 500 ppm showed an increase in pulmonary flow resistance, a decrease in lung compliance, and an increase in the time constant of the lungs and minute volume [Amdur 1961]. At concentrations above 100 ppm, guinea pigs also showed labored breathing and a decrease in respiratory rate [Amdur 1961]. Mice exposed to acetic acid vapor at approximately

1,000 ppm showed signs of conjunctival and upper respiratory tract irritation [Clayton and Clayton 1981]. The oral LD_{50} in rats was 3,530 mg/kg [NIOSH 1991].

2. *Effects on Humans*: In vapor form, acetic acid is a severe irritant of the eyes, mucous membranes, upper respiratory tract, and skin. In contact with the skin or eyes, acetic acid solutions of 80% or more can be corrosive, causing severe burns of any exposed tissue. Long-term exposure to the vapors of this substance causes chronic bronchitis and other respiratory effects, erosion of tooth enamel, and cracking and darkening of the exposed skin.

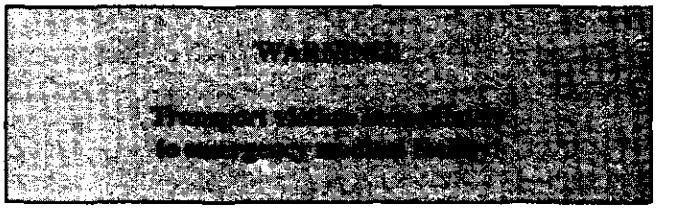
When splashed into the eye, glacial acetic acid has caused permanent corneal opacity; skin contact with glacial acetic acid causes burns and tissue destruction [NLM 1991; AIHA 1978]. Ingestion of corrosive concentrations can cause tissue destruction, perforation, and stricture (delayed) of the throat, esophagus, and stomach; intestinal hemorrhage; and heart and renal damage [NLM 1991]. Unacclimatized individuals have experienced eye irritation at concentrations below 10 ppm, tolerable irritation at 25 ppm, and intolerable eye, nose, and throat irritation at 50 ppm [Proctor et al. 1988]. Exposure at 800 to 1,200 ppm becomes intolerable within 3 min of exposure [ACGIH 1991a]. Five workers who had been exposed to acetic acid vapor at 80 to 200 ppm for 7 to 12 years had thickening and blackening of the skin on the hands, eye inflammation, dental erosion (of both canines and incisors), and chronic pharyngitis and bronchitis [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acetic acid vapor can cause redness, inflammation, lacrimation, runny nose, sore throat, coughing, bronchitis, pulmonary edema, labored breathing, and dyspnea. Death can result from circulatory collapse, renal failure, or glottic edema. Skin contact with concentrated solutions of acetic acid produces redness, blistering, and deep burns; these signs may be delayed for as long as 4 hr after contact. Eye contact with concentrated solutions of acetic acid causes immediate pain and tearing, redness, photophobia, and corneal opacities; if the exposure is severe, vision may be permanently impaired. In addition, ingestion can produce throat, esophageal, and gastric irritation, corrosion, stricture, and perforation; nausea; vomiting; diarrhea; hemorrhage; and shock.

2. *Chronic exposure*: Acetic acid vapors can cause sore throat, coughing, difficult breathing, decrements in pulmonary function, and erosion of the enamel on the incisors and canine teeth. Skin sensitization has rarely been reported. Long-term exposure of the skin to acetic acid vapor may cause it to darken, thicken, and crack.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetic acid! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetic acid are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetic acid or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures

(e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acetic acid and may result in worker exposures to this substance:

—Production of cellulose acetate, vinyl acetate, inorganic acetates, organic acetates (esters), acetic anhydride, chloroacetic acid, ethyl alcohol, ketene, methyl ethyl ketone, acetone, acetanilide, and acetyl chloride

—Use of acetic acid in the dyeing, pharmaceutical, canning, fermentation, and food-preserving industries; in pigment production; and in the tanning of rubber

—Use of acetic acid as a solvent in the liquid-phase oxidation of p-xylene to terephthalic acid, as a fungicide, and as an insecticide

—Use of acetic acid in the production of plastics and photographic chemicals, as a natural latex coagulant, as an oil-well acidizer, in textile printing, as a laundry sour (neutralizer), and as a solvent for gums, resins, volatile oils, and other substances

—Use of acetic acid in the manufacture of Paris green, white lead, and rinse and stain removers

The following methods are effective in controlling worker exposures to acetic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, teeth, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with keratoconjunctivitis or other eye disorders, skin allergies or other skin disorders, erosion of tooth enamel, or respiratory disorders.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employ-

ment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetic acid on the eyes, skin, teeth, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetic acid is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 270 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. The limit of detection for this procedure is 0.01 mg/sample. This method is an OSHA modification of Method 1603 from the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Acetic acid can be absorbed through the skin in toxic amounts, and concentrated solutions of this substance can also cause skin burns. Therefore, if acetic acid contacts the skin, workers should immediately rinse the affected areas with large amounts of water for a minimum of 15 min.

Clothing and shoes contaminated with acetic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the corrosive properties of acetic acid.

A worker who handles acetic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetic acid is handled, processed, or stored.

STORAGE

Acetic acid should be stored in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area should be detached and should be well-ventilated and have acid-resistant floors. The temperature of the storage area should be maintained above 16.7°C (62°F) to prevent rupturing of the containers. Electrical fixtures in the storage area should be vaporproof, and any tools used should be of the nonsparking type. Containers of acetic acid should be protected from physical damage and should be stored separately from oxidizing agents, combustible materials, heat, sparks, and open flame. Because empty containers may contain acetic acid residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. If the vapor from the spill has not ignited, use water spray to reduce the vapors and to protect workers attempting to stop the leak.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the acetic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetic acid is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for acetic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetic acid is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- ***Respiratory protection program***

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent any possibility of skin contact with acetic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by acetic acid and may provide protection

for periods greater than 8 hr: butyl rubber, Teflon®, and Saranex®. Materials that may withstand permeation for more than 4 but fewer than 8 hr are neoprene, polyethylene, and polyethylene/ethylene vinyl alcohol. Natural rubber, polyvinyl chloride, and Viton® demonstrated questionable protection against permeation by acetic acid. Nitrile rubber and polyvinyl alcohol have demonstrated poor resistance to permeation by acetic acid.

If acetic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetic acid might contact the eyes (e.g., through splashes of solution). Splashproof, gas-tight goggles may also be required to prevent irritation of the eyes from acetic acid vapor. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetic acid. Contact lenses should not be worn if the potential exists for acetic acid exposure.

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