Chemical Safety Data Sheet SD-56

PROPERTIES AND ESSENTIAL INFORMATION

FOR

SAFE HANDLING AND USE

OF

VINYL CHLORIDE

●

ADOPTED 1954

Chemicals in any form can be safely stored, handled or used if the physical, chemical and hazardous properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment, are observed.

MCA MANUFACTURING CHEMISTS ASSOCIATION

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CHEMICAL SAFETY DATA SHEET

VINYL CHLORIDE

SUMMARY

Vinyl chloride is a highly volatile extremely FLAMMABLE compressed gas which is ordinarily handled in liquefied form under pressure. It has a mild anesthetic action in concentrations above 500 ppm. and its vapors are irritating to the eyes.

Precautions necessary in handling the material are detailed in the body of the Safety Data Sheet. Key points to consider for safe handling include:

1. Keep away from heat, sparks and open flame.
2. Provide adequate ventilation.
3. Ground equipment and containers before discharging to reduce danger of ignition from static sparks.
4. In discharging do not heat containers above 50°C. (122°F.). No heat should be applied to tank cars.
5. All equipment should be of steel and have a designed working pressure of at least 100-150 psi.
6. In the event of accidental leaks, spills or whenever excessive vapor concentrations may be encountered only personnel equipped with approved respiratory protection should be permitted in the contaminated area.
7. Chemical safety goggles should be worn when discharging containers or tank cars or whenever there is a danger of the liquid or saturated vapor coming in contact with the eyes.
8. Waste disposal should be away from any source of ignition. Dilute phenolic residues before discharging to sewer.

In case of fire use carbon dioxide or dry chemical extinguishing equipment. In the event of contact with the liquid remove contaminated clothing immediately. For eyes flush immediately with large quantities of water for at least 15 minutes while medical attention is being sought.

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Chemical Safety Data Sheet

VINYL CHLORIDE

Adopted February, 1954

1. NAME

Chemical Names:	Vinyl Chloride Chloroethylene Chloroethene
Common Name:	Vinyl Chloride
Formula:	CH_2CHCl

2. PROPERTIES

2.1 Grade:

Technical with inhibitor. (Purity of sample 99.42%)

2.2 Important Physical and Chemical Properties:*

Boiling Point	—13.8°C. (+7°F.)
Color	Colorless or water white
Corrosivity	Noncorrosive at normal atmospheric temperatures when dry (moisture free). In contact with water at elevated temperatures vinyl chloride accelerates corrosion of iron or steel.
Explosive Limits (Percent by Volume in Air)	Lower 4%; Upper 22%
Flash Point	—78°C. (—108.4°F.), Open-Cup
Hygroscopicity	No
Critical Pressure	52.7 Atmospheres
Critical Temperature	158.4°C. (317°F.)
Deliquescence	No
Ignition Temperature, Autogenous	472.22°C. (882°F.) (Vapors above —60°F.)
Light Sensitivity	Not a factor in handling inhibited vinyl chloride
Melting Point (Freezing Point)	—153.71°C. (—245°F.)
Molecular Weight	62.50
Odor	Sweet smelling gas
Physical State	Gas at ordinary temperature and pressure. Liquid under pressure in cylinders or pressure vessels at room temperature.
Reactivity	Polymerizes readily in presence of air, sunlight, oxygen or heat. This behavior is due to the presence of a double bond. Otherwise vinyl chloride is quite stable.
Specific Gravity	.9121 @ 20°/20°C. (Water = 1.00)
Vapor Density	2.15 (Air = 1.00)
Vapor Pressure	2580 mm. of mercury 20°C. (68°F.)

*Many of the data recorded under this paragraph were determined in the research laboratory of one of the large producers of vinyl chloride and are based on a technical grade material having a purity of 99.42%. Materials from other sources may vary in accordance with the nature of the impurities or the character of the inhibitor present.

2.3 Hazardous Properties

2.3.1 *HEALTH HAZARDS* (See 8. Health Hazards and Their Control)

Aside from the risk of fire and explosion, vinyl chloride presents no other very serious problem in general handling. The presently accepted upper limit of safety as a health hazard is 500 ppm.

2.3.2 *FIRE HAZARD*

Vinyl chloride vapors form flammable mixtures with air at all temperatures above —78°C. (—108.4°F.)

3. USUAL SHIPPING CONTAINERS

3.1 Type and Size

3.1.1 Approved ICC cylinders and tank cars designed to carry liquid gases under pressure and equipped with safety relief devices.

3.1.2 All parts of valve and safety devices in contact with contents of containers must be of metal or other material, suitably treated if necessary, which will not cause formation of any acetylides. A good practice is to dismantle all valves for inspection before each loading. Approved cylinders include ICC-4B300, ICC-4BA300, ICC-3A300, and ICC-3AA300. *Cylinders with brazed seams are not permitted.*

3.1.3 Some types of tank cars are ICC-106A-500, ICC-106A500X, ICC-105A300 and ICC-105A300W. Maximum permitted filling density is 84% for cylinders and for Class ICC-106A cars and for Class ICC-105A cars 87%.

3.1.4 Filling density is defined as the per cent ratio of the weight of chemical in the tank to the weight of water that the tank or cylinder will hold.

3.1.5 ICC Regulations require that vinyl chloride must be inhibited for the purpose of transportation (See 6.2.3).

3.2 Label or Identification

3.2.1 Each container of vinyl chloride (including tank cars) should carry an identifying label or stencil.

3.2.2 The Manufacturing Chemists' Association recommends the following in addition to, or in combination with, any label warnings or other statements required by statutes, regulations, or ordinances:

VINYL CHLORIDE

DANGER! EXTREMELY FLAMMABLE LIQUID AND GAS UNDER PRESSURE

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid prolonged breathing of vapor.

3.2.3 Each shipping container must bear the ICC red label for FLAMMABLE compressed gases.

3.2.4 Tank cars and railroad cars carrying one or more containers of vinyl chloride must bear the ICC DANGEROUS placard.

3.3 Disposal and Return Precautions

3.3.1 Small containers (ICC-4B300 and ICC-4BA300, without brazed seams, ICC-3A300, ICC-3AA300) should be drained free of liquid vinyl chloride and the valves closed tightly before they are returned to the supplier. No air should be permitted to enter the container (See 4.3).

3.3.2 In addition, the following precautions must be taken:

3.3.2.1 *Return of Small Containers*

The cylinder valve protection cap or outlet cap must be securely replaced. The lower portion of the ICC shipping tag, if attached to the cylinder, must be removed. In other cases, applicable to ICC Regulations, compliance is essential. Bill of lading should give the cylinder identification number (which appears on the shoulder of cylinder) for each cylinder shipped, show name of consignee and indicate that the cylinders are empty (See 3.3.5).

Full or partly emptied cylinders should not be returned without permission of the supplier. Such cylinders must be shipped as full cylinders and correspondingly labeled and tagged (See 3.2). All empty cylinders should be returned promptly.

3.3.3 Tank cars (ICC-106A500, ICC-106A-500X, ICC-105A300, and ICC-105A300W) should be drained free of liquid vinyl chloride, the valves should be securely closed and the valve plugs replaced. No air should be permitted to enter the vessel. The inert gas used for the unloading procedures (See 4.4 Tank Cars) should be left in the vessel at a pressure not to exceed the service pressure for which the car is authorized.

3.3.4 In addition, the following precautions must be taken:

3.3.4.1 *Return of Tank Cars*

As soon as a tank car is completely unloaded, all valves must be made tight, the unloading connections must be removed and all closures made tight, except that heater coil inlet and outlet pipes (if any) must be left open for drainage. Heater coils must never be used in unloading vinyl chloride. Empty tank cars should be returned as promptly as possible, in accordance with instructions received from shipper.

3.3.5 Follow ICC Regulations regarding the replacement of closures, condition and labeling of empty containers; condition of empty cars and placard requirements before returning to shipper. The ICC DANGEROUS placards on sides and ends of tank cars must be removed, or reversed (if in metal placard holders) by the party discharging the tank car. The empty car must be offered to the receiving carrier either without placards, or preferably with four (4) DANGEROUS-EMPTY placards.

4. UNLOADING AND EMPTYING

4.1 Health Hazards (See 8. Health Hazards and Their Control)

4.1.1 Aside from the risk of fire and explosion, vinyl chloride presents no other very serious problem in general handling. The presently accepted upper limit of safety as a health hazard is 500 ppm.

4.2 Fire and Explosion Hazards

4.2.1 Vinyl chloride should always be handled with full recognition of its flammability. Precautions should be taken both to keep the material enclosed and to eliminate sources of ignition. Reliance must be placed upon the elimination of all sources of ignition and on the provision of sufficient ventilation to keep escaping vapors at nonflammable levels (See 6.2).

4.3 Cylinders

4.3.1 Precautions generally applied to use of cylinders (ICC-4B300 and ICC-4BA300, without brazed seams, ICC-3A300, ICC-3A-A300) for flammable liquefied gases should be used.

4.3.2 A water bath heated to a maximum of 50°C. (122°F.) may be used to empty cylinders by means of the vapor pressure of the vinyl chloride.

4.3.3 Check valves must be installed in feed lines from the cylinder to prevent the reactants from entering the cylinder.

4.3.4 When the cylinder is empty, the valve should be securely closed. Air should not be allowed to enter the container.

4.3.5 Valve protective caps should be kept in place on cylinders except when the cylinders are connected for discharge.

4.3.6 Cylinders must not be filled except by or with the consent of the owner, and then only in accordance with the Regulations of the Interstate Commerce Commission.

4.3.7 No attempt should ever be made to mix gases or liquids in a cylinder.

4.4 Tank Cars

4.4.1 Applicable instructions for unloading tank cars containing flammable liquids are set forth in MCA Manual Sheet TC-4. (Also see ICC Regulations, Sec. 74.560 to 74.563 inclusive, for unloading tank cars.)

4.4.2 Shipper's instructions should always be followed and all caution markings on both sides of tank and dome should be read and observed.

4.4.3 In the event of a tank car fitting failure or leak, the shipper should be telephoned or wired immediately for instructions (See 6.3).

4.4.4 Tank cars should be electrically grounded to dissipate static or induced lightning charges.

4.4.5 No heat should be applied to the tank car. An inert gas line or compressed vinyl chloride gas line should be attached to vent connection of the tank car to provide a pressure for transfer of the liquid vinyl chloride from tank car to receiving tank.

Cylinder nitrogen (inert gas) is often used as the pressuring medium in the event vinyl chloride gas is not available. Larger installations may have a suction line connected from the storage tank to a compressor which discharges compressed vinyl chloride gas to vent connection on tank car. The pressure on the car should never exceed the service pressure at which the safety valve is set to operate.

4.4.6 Some tank cars in vinyl chloride service are equipped with excess flow check valves. A too rapid opening of the discharge valves will cause the check valves to close. If this should occur, the outlet valve should be closed until the pressure is equalized and the excess flow valve opens.

4.4.7 Positive vinyl chloride or inert gas pressure should be left in car. No air should be allowed to enter car (See 3.3.3).

5. STORAGE

5.1 Hazards (See 8. Health Hazards and Their Control)

5.1.1 Aside from the risk of fire and explosion, vinyl chloride presents no other very serious problem in general handling. The presently accepted upper limit of safety as a health hazard is 500 ppm.

5.1.2 Vinyl chloride should always be handled with full recognition of its flammability. Precautions should be taken both to keep the material enclosed and to eliminate sources of ignition. If there should be any unavoidable leaks, reliance must be placed upon the elimination of all sources of ignition and on the provision of sufficient ventilation to keep escaping vapors at nonflammable levels (See 6.2).

5.1.3 *CORROSION*

Vinyl chloride is noncorrosive at normal atmospheric temperatures when dry (moisture free). In contact with water at elevated temperatures vinyl chloride accelerates corrosion of iron or steel.

5.1.4 *VOLATILITY*

Vinyl chloride is very volatile and is a gas at normal atmospheric conditions. Containers used for handling vinyl chloride at atmospheric temperature are always under pressure.

5.1.5 *TEMPERATURE REQUIREMENTS*

Inhibited vinyl chloride may be stored at normal atmospheric conditions in suitable pressure vessel.

Uninhibited vinyl chloride may be stored either under refrigeration or at normal atmospheric temperature in the absence of air or sunlight but only for a duration of a few days. If for longer periods, regular checks should be made for the presence of polymers.

5.2 Conditions of Storage

5.2.1 *TYPE OF CONSTRUCTION*

All piping (including instrument leads), storage tanks, relief devices and equipment employed to handle vinyl chloride should be of steel and designed to have a working pressure of at least 100-150 psi with a safety factor conforming to the A.S.M.E. code for unfired pressure vessels or any code applying to locale of planned storage. Shut-off valves and control

valves should be of steel or a suitable alloy not bearing copper, designed for working pressures of 150 psi or over. All-welded construction is preferred to riveted construction. It is recommended wherever possible that all liquid inlet lines enter the bottom or extend to the bottom of the vessel. This guards against the accumulation of static electricity. All equipment should be properly grounded with resistance to ground never exceeding 25 ohms. An efficient water spray system should be installed or made available. Adequate diking and drainage should be provided under tank area to confine and dispose of the liquid in case of vessel rupture. Any cylinders used to store vinyl chloride must meet ICC Specifications.

5.2.2 *ISOLATION*

Storage areas should be selected in accordance with local codes or authorities having jurisdiction. (Assistance may be obtained from such organizations as National Board of Fire Underwriters, Factory Insurance Association, Associated Factory Mutual Fire Insurance Companies.) For highly volatile and flammable material, storage should be located outside of buildings. Cylinders containing vinyl chloride should be stored always in a vertical position, outside of buildings, and in an isolated and well ventilated area. It is preferable to store cylinders in the open, but provision should be made to shield them from the direct rays of the sun and prevent accumulation of dirt, snow, water, or ice on valves or safety devices.

5.2.3 *COMPATIBLE AND DANGEROUSLY REACTIVE MATERIALS*

Tanks in vinyl chloride service should be used only for the storage of vinyl chloride (See 6.8). Before vinyl chloride is placed in a tank, the vessel should be purged with an inert gas until free of air. Vinyl chloride is generally noncorrosive at normal atmospheric temperatures when dry (moisture free). However, mild to appreciable corrosion has been noted even at ordinary temperature. This may be due to the presence of impurities. In contact with water at elevated temperatures vinyl chloride accelerates corrosion of iron or steel. Acetylene as an impurity in vinyl chloride may form an explosive compound (acetylide) when exposed to copper or possibly copper alloys.

5.2.4 *VAPOR-PROOF OR EXPLOSION-PROOF REQUIREMENTS*

All electrical equipment, motors, lights, and flashlights used in an area in which vinyl chloride is stored or handled should conform to the National Electrical Code (Class I, Division II for storage; and Class I, Division I for use).

5.2.5 *VENTING REQUIREMENTS*

An adequate system for normal and emergency venting should be installed. All vent lines should extend to a safe area free of any source of ignition. The point of outlet should be equipped with an approved flame arrestor. Relief valves should be installed in pairs, parallel, using transflow valving to facilitate periodic testing and repairing.

5.2.6 *VENTILATION*

All storage areas should be provided with continuous ventilation. Pits, depressions and basements should be avoided.

5.2.7 *PROTECTION FROM ELECTRICAL STORMS*

Storage tanks for vinyl chloride should be protected from electrical storms and induced static electricity by grounding of all equipment.

5.2.8 *PROTECTION FROM INTERNAL EXPLOSIVE MIXTURES*

Storage tanks and other vessels should be maintained under positive pressure utilizing an inert gas when necessary or vapor pressure of the vinyl chloride. Vessels should be provided with bottom inlets under the liquid, or dip pipe extending from the top of the vessel to within inches of the bottom of the vessel to protect against a static discharge.

6. HANDLING

6.1 **Health Hazards** (See 8. Health Hazards and Their Control)

6.1.1 Aside from the risk of fire and explosion, vinyl chloride presents no other very serious problem in general handling. The presently accepted upper limit of safety as a health hazard is 500 ppm.

6.2 **Fire, Explosion, and Polymerization Hazards**

6.2.1 *FIRE HAZARDS*

Vinyl chloride should always be handled with full recognition of its volatility and its flammability. In general, precautions should be taken both to keep the material enclosed and to eliminate all sources of ignition. In small

laboratory operations, where vinyl chloride vapors may escape, reliance must be placed upon the elimination of sources of ignition and the provision of sufficient ventilation to keep escaping vapors at non-flammable levels. Vinyl chloride vapors can form flammable mixtures with air at all temperatures above —78°C. (—108.4°F.).

Fires involving large quantities of liquid are difficult to extinguish since vinyl chloride is not miscible with water and is lighter than water (will float on top of water). Most small fires can be extinguished with carbon dioxide or dry chemical agents if properly applied. Adequate fire extinguishing equipment of carbon dioxide or dry chemical type, fixed and portable, should be provided. Water spray is also satisfactory for extinguishing fires. Diking and drainage should be provided for confining and disposing of the liquid in case of tank rupture or spills. Precautions should be taken to guard against vinyl chloride entering general sewer system (See 6.3).

In event of a fire no unauthorized person should be permitted to enter an unventilated area until the space has been thoroughly sprayed with water to remove gases such as hydrogen chloride, phosgene, carbon monoxide, etc. generated from the fire.

6.2.2 *EXPLOSION HAZARDS*

Vinyl chloride is a gas at normal atmospheric temperature and pressure. The gas will burn very readily in proper mixtures of air or oxygen. The explosive limits are: lower 4.0%, upper 22.0% by volume in air. An explosion hazard can exist when drawing samples or venting to the atmosphere. Open flames, local hot spots, friction, any spark producing equipment, and static electricity are to be avoided when handling this material.

6.2.3 *POLYMERIZATION HAZARDS*

Vinyl chloride does not form peroxides by autoxidation as readily as many other monomers. Aside from polymerization, vinyl chloride is chemically quite stable (See 2.2 Reactivity). Vinyl chloride can be satisfactorily stored without an inhibitor for short periods if it is kept in steel tanks under refrigeration or at normal atmospheric temperature in the absence of air and sunlight. For shipping purposes inhibitors are employed. Inhibitors, like phenol, when present have hazards of their own, being very toxic (See 7.5).

6.3 Spills and Leakage

6.3.1 Frequent inspections of equipment and vessels containing vinyl chloride should be made to detect or prevent leaks.

6.3.2 If spills or leaks occur, all sources of ignition if required to be present in the area and adjacent areas must be shut off immediately. Only necessary and properly protected personnel should remain in the area (See 6.5).

6.3.3 Spills, unless very large, usually evaporate rather rapidly and do little damage, but ample ventilation should be provided to prevent the formation of toxic and explosive mixtures. Spills should be guarded and controlled immediately. All openings in sewer system should be trapped for segregation and extinguishment. All sources of ignition should be removed (See 6.2.1).

6.3.4 If possible, increased forced ventilation should be provided. Inhalation of vapors should be avoided (See 8).

6.3.5 Leaking cylinders in any enclosure should be removed to an isolated, well-ventilated area and the contents transferred to other suitable containers (See 4.3 and 5.2.2).

6.3.6 The detection of leaks in equipment of vinyl chloride can best be accomplished by the use of a flammable gas indicator, or by inspection for the presence of vapors and frosting on the surfaces of the equipment.

6.3.7 In the event of a tank car leakage, utilize necessary personal protective equipment and make emergency repairs, if possible. The supplier should be telephoned or wired immediately for specific instructions. Guard against the fire hazard or explosion hazard (See 6.2).

6.3.8 Clothing contaminated with vinyl chloride should be removed immediately and the body washed thoroughly to remove any material which may have penetrated to the skin. Clothing should be washed before reuse. If necessary shoes should be replaced with new ones. Disposal of the contaminated shoes is recommended if the spilled vinyl chloride contained a toxic inhibitor, like phenol.

6.4 Employee Education and Training

6.4.1 Safety in handling vinyl chloride and other hazardous chemicals depends upon the effectiveness of employee education, training, and the safety instructions incorporated into job instruction manuals.

6.4.2 The education and training of employees to work safely and to use the personal protective equipment or other safeguards provided for them is a responsibility of supervision.

6.4.3 Employee education and training should emphasize the need of handling vinyl chloride according to the methods outlined in this data sheet.

6.4.4 Before being placed on the job, new or transferred employees should be thoroughly instructed and questioned in respect to the proper handling of vinyl chloride. Employees on the job should be reinstructed periodically.

6.4.5 Each employee should know the location, purpose, use and maintenance of personal protective equipment and be thoroughly trained in when and how to use the equipment (See 6.5).

6.4.6 Each employee should know the location of safety showers, eye baths, bubbler drinking fountains, faucets or fire extinguishing equipment.

6.4.7 Only reliable, properly trained employees should be given the responsibility of operating valves which control the flow of vinyl chloride to and from storage tanks, tank cars, and cylinders, or drawing samples and venting to the atmosphere.

6.4.8 Employees should be trained to report to the proper authority all suspected leaks or equipment failures and any signs of illness of personnel.

6.4.9 Each employee should know what to do in case of an emergency, in rendering first aid measures, and should realize the necessity for prompt administration of artificial resuscitation when overcome by vinyl chloride vapors (See 8.4.2.1).

6.5 Personal Protective Equipment

6.5.1 *AVAILABILITY AND USE*

Personal protective equipment is not an adequate substitute for good, safe, working conditions, adequate ventilation, and intelligent conduct on the part of employees working with vinyl chloride. Such equipment may protect the individual wearing it while others in the area may be exposed to danger. The correct usage of personal protective equipment requires the education of the worker in the proper employment of the equipment available to him (See 6.4). Under conditions which are sufficiently hazardous to require protective equipment, the use of it should be supervised. In all cases, the type of protective equipment selected should depend upon the nature and degree of the hazards existing.

The following personal protective equipment should always be used for the purposes mentioned and as specified in Section 8. Health Hazards and Their Control, and in other sections of this data sheet:

6.5.2 *EYE PROTECTION*

6.5.2.1 *Chemical Safety Goggles:* cup-type or rubber-framed goggles, equipped with approved impact resistant glass or plastic lenses, should be worn whenever there is danger of the vinyl chloride (in liquid or saturated vapor form) coming in contact with eyes. Goggles should be carefully fitted by adjusting the nose piece and head band to ensure maximum protection and comfort.

6.5.2.2 *Spectacle-type Safety Goggles:* metal or plastic rim safety spectacles with perforated side shields which can be obtained with prescription safety lenses or suitable all plastic safety goggles may be used where continuous eye protection is desirable. These types, however, should not be used where complete eye protection against chemicals is needed.

6.5.2.3 *Face Shields:* plastic shields (full length, eight inch minimum) with forehead protection may be worn in lieu of, or in addition to, chemical safety goggles where complete face protection is desirable. Chemical safety goggles should always be worn as added protection where there is danger of vinyl chloride striking the eyes from underneath or around the sides of the face shield.

6.5.2.4 Each employee should know the location of safety showers, eye baths, and bubbler drinking fountains for flushing the eyes.

6.5.3 *RESPIRATORY PROTECTION*

Respiratory protective equipment must be carefully maintained, inspected, cleaned, and sterilized at regular intervals, and always before use by another person. Personnel wearing such equipment must be carefully instructed as to its operation and limitations.

6.5.3.1 *Air or Oxygen Supplied Masks*

6.5.3.1.1 Air or oxygen supplied masks, equipped with full face pieces and approved by the U. S. Bureau of Mines for this purpose, should be used under the following conditions,

and the manufacturer's instructions must be carefully followed:

(a) In emergencies, when the vapor concentration is not definitely known.

(b) When the harmful vapor concentration is over 2 per cent by volume.

(c) When the oxygen content of the air may be less than 16 per cent by volume.

(d) When the exposure period is to be over 30 minutes duration.

(e) In tank and equipment cleaning and repair work under conditions outlined in (a), (b), (c) and (d).

6.5.3.1.2 *Types Generally Available Include:*

(a) *Air-Line Masks* supplied by plant compressed air are suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply. Such masks should be used only in conjunction with a suitable reducing or demand-type valve, excess pressure relief valve, and filter. The compressed air should be checked frequently to make certain that harmful gases from the decomposition of the lubricating oil used in the compressor, or impure air supply, are not present.

(b) *Positive Pressure Hose Masks* supplied by externally lubricated blowers are usually preferred to the air-line type. Since these masks also depend on a remote air supply, they should be used only where conditions will permit safe escape in the event of air supply failure. Care must be taken to locate the blower air source in an area which is free of air contaminants.

(c) *Self-contained Breathing Apparatus* which permits the wearer to carry a supply of oxygen or air compressed in the cylinder, and the self-generating type which produces oxygen chemically, allow for greater mobility. The length of time a self-contained breathing apparatus provides protection varies according to the amount of air or oxygen supply carried. In tank work, where small manholes are encountered, a self-contained breathing apparatus is usually unsuitable because of its bulk.

6.5.3.2 *Industrial Canister Type Gas Masks* equipped with full face pieces and approved by the U. S. Bureau of Mines, fitted with the proper canister for absorbing vinyl chloride vapor (or gas), will afford protection against concentrations not exceeding 2 per cent by volume when used in accordance with the manufacturer's instructions. The oxygen content of the air must be not less than 16 per cent by volume. The masks should be used for relatively short exposure periods only, i.e., less than 30 minutes. They may not be suitable for use in an emergency since, at that time, the actual vapor concentration is unknown and it may be very high. The wearer must be warned to leave the contaminated area immediately on detecting the odor of vinyl chloride. This is an indication that the mask is not functioning properly or that the vapor concentration is too high.

NOTE: Where carbon monoxide may be encountered in addition to vinyl chloride, the mask should be equipped with an "All Purpose Canister" and a "Timing Device" as approved by the U. S. Bureau of Mines.

6.5.3.3 *Chemical Cartridge Respirators* approved by the U. S. Bureau of Mines may be used to avoid inhaling disagreeable but harmless concentrations of vinyl chloride vapor. These respirators, however, are not recommended for protection where toxic quantities of an air contaminator may be encountered.

6.5.4 *HEAD PROTECTION*

6.5.4.1 Safety or "hard" hats will provide protection against accidental liquid leaks, falling tools, and other objects.

6.5.4.2 Brimmed felt hats may be substituted for a safety hat where danger of falling objects is remote.

6.5.5 *FOOT PROTECTION*

High leather or synthetic rubber safety shoes with built-in steel toe caps are recommended where there is danger of heavy objects falling on workman's foot. Liquid vinyl chloride penetrates leather, and shoes wet with vinyl chloride should be replaced.

6.5.6 *BODY, SKIN AND HAND PROTECTION*

6.5.6.1 Any work gloves, clothing or wearing apparel which becomes contaminated with vinyl chloride should be removed immediately, and the body should be thoroughly washed. All contaminated work gloves, clothing or wearing apparel should be thoroughly washed, and dried before reuse. For care of contaminated shoes see 6.5.5.

6.5.6.2 When cleaning, inspecting, or repairing tanks, safety equipment such as safety

belts, rescue harness, lifeline, clothing and gas masks should be worn as required by the specific nature of the work and the hazards involved.

6.5.6.3 Frequent inspections and necessary repairs should be made to all personal protective equipment so that it is always ready to give proper protection to the wearer.

6.5.6.4 Facilities for personal cleanliness should be provided and time allowed for thorough washing before lunch and at the end of the work day.

6.6 Engineering Controls

6.6.1 Selection of a site or location for apparatus or equipment to ship, handle, store or manufacture vinyl chloride should be made by the direction of chemical engineers or mechanical engineers fully aware of the hazards encountered in dealing with vinyl chloride (See 5.2.2).

6.6.2 Processes should be designed so that the operating personnel will not be exposed to direct contact with vinyl chloride or its vapor. The technical problems of designing equipment, providing adequate ventilation, and formulating operational procedures which promise maximum security and economy, can be handled best by engineers or other competent personnel. The manufacturers of vinyl chloride, and of the equipment in which it is to be used, are always prepared to help with these problems (See 5.2.1).

6.6.3 In the handling of vinyl chloride or operation of any type of vinyl chloride system, all valves, pipe lines, vents, safety devices, etc., should be so located that they can be readily inspected and repaired. They should always be in proper order and condition before the operation is started. All handling and storage equipment should be located away from any source of sparks, flames, heated surfaces and all sources of ignition which might cause fires or explosions. All charging and discharging pipes should enter through, or extend to, the bottom of all containers to minimize vaporization of the liquid and possible generation of static electricity.

6.6.4 It is essential for safety that equipment will be used and maintained as recommended by the manufacturer and that a periodic test schedule of the equipment, including safety devices, should be followed. All vent lines should extend outdoors to an area free of any source of ignition for discharge.

6.6.5 All electrical installations should conform with the National Electrical Code. All equipment should be properly grounded to prevent accumulation of static.

6.7 Ventilation

6.7.1 If the workroom or operating area is separate from vinyl chloride storage or processing equipment, general ventilation is adequate. For emergencies, however, the area should be provided with mechanical exhaust ventilation to maintain concentrations below flammable limits.

6.7.2 In the processing or storage area, if outside location is impracticable, special emergency equipment for ventilation is necessary under abnormal conditions, such as leaks or spills.

6.7.3 Six or more changes of air per hour are considered adequate for buildings housing storage or processing equipment for flammable liquids, vapors, or gases under pressure.

6.7.4 Buildings of substantial construction should have at least one square foot of door, window, or nonrigid roof area for each 35 cubic feet of volume to prevent serious structural damage in the event of explosion within the building.

6.7.5 The most important consideration in ventilation is to ensure an adequate air flow away from the work area.

6.7.6 All ventilating systems should be inspected periodically and maintained in a safe and efficient working condition.

6.7.7 Under abnormal conditions, such as when leaks or spills occur, all available ventilation should be used.

6.8 Tank and Equipment Cleaning and Repairs

6.8.1 The hazardous nature of tank or vessel inspections, cleaning, and repairs requires that the foreman and crew be selected, trained, and drilled carefully. They should be fully familiar with the hazards and safeguards necessary for the safe performance of the work. Use only spark-resistant tools.

6.8.2 Wherever possible, vessels should be cleaned from the outside, using cleanout manholes or openings provided for this purpose.

6.8.3 First consideration in vessel entry work requires the vessel be properly isolated

from any process equipment, pipe lines, or apparatus. These process lines, pipe lines, and apparatus should be disconnected, preferably by removing a complete small section and providing a blank flange on the open end to protect against human error and unsuspected leaks. Valves and plug cocks in the process lines, pipe lines, or apparatus should not be relied upon to prevent leakage into vessel being cleaned.

6.8.4 Electrical switches should be locked in the "OFF" position and tagged with a warning that they are not to be opened. Where possible, the fuses should be pulled. Drive belts should be removed and all other precautions taken to ensure against the accidental starting of agitating equipment or other moving parts inside the vessel or adjacent to the entrance.

6.8.5 Before entering a tank, it should be empty, purged, and tested for flammable residues. Caution should be exercised in checking for trapped vapors in any semi-solid or solid residues. In purging a vessel, an inert gas (carbon dioxide or nitrogen) is recommended. The inert gas must be displaced before allowing entry into a vessel. When air is used for purging a vessel, there is a period when an explosive mixture is present (mixture contains by volume between 4-22% gas). For this reason it is best to avoid the use of air in removing flammable vapors.

6.8.6 Warning signs should be placed indicating nature of hazard present during preparation of vessel for entry or repair.

6.8.7 Before entering a vessel and during the course of the work, tests should be made by a qualified person to determine that no further purging or washing is necessary, that no oxygen deficiency exists, and that no harmful gas or vapor is present.

6.8.8 Special ventilation and a continuous fresh air purging of vessel is recommended during the entire time men are cleaning, inspecting, or repairing vessel.

6.8.9 Proper personal protective equipment such as a safety belt, rescue harness, lifeline, or mask as required should be worn by anyone entering a vessel after preparation for inspection, and/or repairs (See 6.5).

6.8.10 An attendant should be stationed outside the vessel in such a position as to keep workmen within the vessel under constant observation. He should serve as the lifeline tender and be ready at all times to summon help or other required aid. He should never abandon the lifeline while workmen are in the vessel.

6.8.11 A self-contained breathing apparatus or an air-supplied mask should be located immediately adjacent to vessel repair area for any emergency situation during vessel entry work. In addition a lifeline and safety harness should be on hand.

6.8.12 The portable electric lights and power tools should be in good condition, grounded and approved by competent persons for use in exposures of this nature.

6.8.13 Before reuse, the vessel should be purged free of air by using an inert gas such as carbon dioxide or nitrogen.

6.9 Repackaging

6.9.1 Only clean, ICC Specification cylinders or tank cars should be used (See 3.1).

6.9.2 Adequate ventilation should be provided and all sources of ignition removed from transfer area.

6.9.3 Proper personal protective equipment should be used (See 6.5). Transferring vinyl chloride from cylinders by the use of an uncontrolled heating method is not recommended because it is unsafe, wasteful, and time consuming. Temperatures of over 50°C. (122°F.) should not be applied to any part of a cylinder containing compressed gas. Excessive heating weakens the structural characteristics of the metal and may seriously damage the cylinder. Low melting safety devices may reach the fusing point by the application of excessive heat to a cylinder. Never apply direct flame to a cylinder. A definite fire hazard is created. For recommended practice to transfer contents of a cylinder see 4.3.

6.9.4 For recommended practice to transfer contents of tank car see 4.4.

6.9.5 The appropriate labels should be applied to the filled cylinders or tank cars (See 3.2).

7. WASTE DISPOSAL

7.1 All Federal, State, and local regulations regarding health and pollution should be observed. Disposal of waste material, however, depends to a great extent upon surroundings and weather conditions.

7.2 When it becomes necessary to dispose of vinyl chloride as such, it is preferable to do so as a vapor, venting to an area free of any source of ignition (See 5.2.5 and 5.2.6).

7.3 When a waste disposal problem arises as a result of a major spill or equipment rupture, only properly protected and qualified personnel should remain in the area (See 6.3 and 6.5).

7.4 Waste mixtures containing vinyl chloride should not be allowed to enter drains or sewers as serious explosion in such systems may result (See 6.3).

7.5 Removal of inhibitor, such as phenol in form of sodium phenolate, should be done by dilution to approximately 1% solution (See SD-4, Part 7. Waste Disposal).

8. HEALTH HAZARDS AND THEIR CONTROL

8.1 Hazards

8.1.1 *GENERAL*

Aside from the risk of fire or explosion, vinyl chloride presents no other very serious problem in general handling. The presently accepted maximum allowable concentration is 500 ppm.

8.1.2 *SYSTEMIC EFFECTS*

In concentrations well above 500 ppm. vinyl chloride acts as a mild general anesthetic.

8.1.3 *LOCAL EFFECTS*

In contact with the skin vinyl chloride *is irritating*. Prolonged contact will result in refrigeration and freezing.

8.2 Prevention and Control

Vinyl chloride is not a serious industrial hazard provided precautions are taken to avoid leaks or spills which might provide a fire or explosion hazard. Where serious leaks or spills do occur, the workmen present in the area should be evacuated, and persons returning to the area to repair or clean up equipment should be provided with appropriate gas masks, self-contained oxygen units, or air supplied hoods.

8.2.1 *EMPLOYEE EDUCATION* (See 6.4 Employee Education and Training)

Employees working in areas where vinyl chloride is handled or stored should be thoroughly and repeatedly warned of the anesthetic properties of vinyl chloride gas and instructed as to what to do if anesthetic effects are detected in themselves or in others (See 8.4.2.1).

Emphasis in training should be placed on:

1. *The use of artificial respiration in cases where breathing has stopped because of deep anesthesia.*
2. *The necessity of immediate removal of contaminated clothing and shoes in case of liquid spills.*
3. *Repeated washing of the eyes with copious amounts of water in case of liquid splashes.*

8.2.2 *VENTILATION*

Work areas where vinyl chloride is handled or stored should be provided with adequate ventilation. The concentration of vinyl chloride should be kept below the upper safe limit of 500 ppm. at all times.

8.3 Personal Protective Equipment

8.3.1 No personal protective equipment is an adequate substitute for safe working conditions and intelligent conduct on the part of employees who work with vinyl chloride. Furthermore, the correct usage of personal protective equipment requires education of the worker in the proper employment of the materials available to him. Under conditions which are sufficiently hazardous to require personal protective equipment, the use of it should be supervised.

8.3.2 Employees who may be subjected to severe exposure to vinyl chloride, as in tank and equipment cleaning and repairs, in decontaminating extensive areas after large spillage, or in cases of failure of piping or equipment, should be provided, when indicated, with proper eye, respiratory, skin, and mucous membrane protection as follows:

(a) Suitable gas tight safety goggles.

(b) Rescue harness and life line for those entering tank or enclosed storage space (See 6.7).

(c) Hose masks with hose inlet in a vapor-free atmosphere, air line masks with proper reducing valve and filter, suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply, or self-contained breathing equipment with stored oxygen or air (such equipment allows greater mobility but usually requires more highly trained men).

8.3.3 Facilities for washing eyes and skin with large quantities of water should be readily available (See 6.5.2.4).

8.4 First Aid and Medical Care

8.4.1 *GENERAL PRINCIPLES*

8.4.1.1 As in exposure to any odorless or mildly scented anesthetic gas, a recognition of the presenting symptoms and signs in oneself and in others is very important. The anesthetic properties of vinyl chloride are mild in degree and slow in developing. Detection of symptoms except in very high concentrations permits ample warning and sufficient time for escape from the environment provided the warning is heeded and escape is possible.

8.4.1.2 As in any skin contact with irritating or harmful materials, speed in removing the contaminant from the skin is of primary importance. Vinyl chloride is very volatile and simple exposure to air will usually effect adequate removal. Clothing, shoes, bandages, or other articles by which vinyl chloride might be held in contact with the skin should be immediately removed to decrease the freezing effect.

8.4.2 *SPECIFIC ACTIONS*

8.4.2.1 *Inhalation*

Continued exposure to atmospheres containing vinyl chloride in concentrations of 1000 ppm. or over will slowly produce evidences of mild anesthesia: (1) a sensation of drowsiness and inability to concentrate, (2) a blurring of vision—at first readily cleared by conscious effort—later controlled only with difficulty or not at all, (3) staggering gait, (4) sensation of numbness or tingling in feet or hands or both.

These symptoms may be readily detected by the employee himself if he has been alerted to the possibility of their arising from overexposure to vinyl chloride. They may also be noted in fellow employees. When such symptoms arise, they are definite warning of a hazardous exposure to vinyl chloride, and all personnel should be immediately evacuated from the area until the leak or spill has been located and corrected and until complete recovery from all symptoms has occurred.

Because of the mildness and slow development of symptoms, it is very unlikely that any workman will be overcome to the point where he will require help in escaping the environment or medical care following exposure. Any person with evidence of intoxication from vinyl chloride should be put at rest, either seated or lying, in an uncontaminated atmosphere.

If trapped in an area of high concentration where escape is impossible, deep anesthesia can result. If such an exposure has occurred, the patient should be placed in bed, preferably with the head slightly lowered and with no pillows. If respirations have ceased, artificial respiration will be required. In any case, medical attention should be obtained immediately.

8.4.2.2 *Contact with Skin*

Liquid vinyl chloride is a primary irritant to intact skin. If sufficient quantities remain long enough in contact with the skin, the rapid evaporation may result in freezing or "frost bite". Consequently, anything which tends to hold vinyl chloride in contact with the skin, such as clothing, shoes, or bandages, increases the risk of freezing.

If spills occur, all contaminated clothing should be removed immediately and the contaminated area washed copiously in running water. If mild irritation has occurred, no further treatment may be required. If inflammation is severe, loose dressings of petroleum jelly should be applied and the patient placed in the care of a physician.

If freezing has occurred, the area should be loosely covered with a clean, preferably sterile, gauze or towel and placed in the care of a physician.

8.4.2.3 *Contact with Eyes*

Vinyl chloride which has gotten into the eyes should be washed out immediately with copious amounts of flowing water. Water at room temperature will produce less pain than very cold water, but in an emergency a drinking fountain is a satisfactory source of water. The washing should continue for at least 15 minutes. If injury is apparent in the tissues of the eye after 15 minutes of irrigation, the washing should be continued for another 15 minutes. In all cases except of very minor irritation, the patient should be placed in the care of an ophthalmologist immediately.

The medical information in this publication has been supplied by the Medical Advisory Committee of the Manufacturing Chemists' Association, Inc.

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Toxicology of Plastics and Rubber

—PLASTOMERS AND MONOMERS

REX H. WILSON, M.D., F.A.C.P., and WILLIAM E. McCORMICK, M.S.
The B. F. Goodrich Company, Akron, Ohio

THE POPULAR demand for all types of articles made from plastics has been so tremendous that literally there has been created an entirely new industry in the past several years. Many plants, large and small, are devoting their entire manufacturing facilities to "plastic" items. The demand for the compounds going into the composition of the plastic materials is so great that supplies of certain of them are short.

Because the industry is new and because of the ingenuity of modern research, the compounds making up the plastics are ever changing. Also, as demands for different types of articles made from plastics are increasing, this creates a demand for different types or kinds of plastics (Table I). Naturally, the kind of material needed for a plastic automobile body is different from the material needed for an elastic garden hose or a pair of stockings. I know of no other industry which better represents the creative genius of man than the so-called plastic industry. The creation at less cost of better things for better living is the aim of the modern business man. To achieve this, there have been brought into existence the wonderful modern-day research laboratories.

It is important to know the chemical properties of a compound and its toxicity. It is also important to know how to work with it safely. Equally important is to know the treatment for overexposure to the toxic chemical to prevent permanent damage or death.

It would be impossible to name, let alone discuss, the toxicological properties of all of the chemical compounds being used in the plastic industry. It is worth-while to discuss the properties of some of the more common resins, plasticizers, stabilizers and solvents being used. Unfortunately, the toxicological properties of all of these are not too well defined. It is to the credit of people working in industrial medicine and hygiene that industry is becoming aware of the necessity for knowing the toxicity of its materials and is taking steps to insure that its employees are not exposed to materials that would harm them.

Presented at the Eleventh International Congress on Industrial Medicine, Naples, Italy, September 13-19, 1954.

Resins

LEHMAN[1] in July, 1951, presented a list of resins both suitable and unsuitable for use as food packaging ingredients. He stated "that as a general rule resins are so insoluble as a class that the chances of contamination by the solvent action of foods are rather slight." The types of resins he considered suitable for food use are:

Polyvinyl chloride.
Polyvinyl acetate.
Polyvinyl chloride-acetate.
Polyvinylidene chloride.
Polystyrene.
Polyethylene.
Cellulose acetate.
Regenerated cellulose.
Terephthalic acid-ethylene glycol copolymer.
Butadiene-acrylonitrile (Perbunan or Hycar synthetic rubber).

Lehman classified as being unsuitable for use in food packages because of the lack of adequate data concerning their toxicity:

Polyvinyl formal.
Polyvinyl acetal.
Polyvinyl butyral.
Polymeric furfuryl alcohol.
Coumarone-indene.
Urea formaldehyde.
Phenol formaldehyde.
Aniline formaldehyde.

A. Vinyl Type

VINYL CHLORIDE, vinylidene chloride, and vinyl acetate readily polymerize. By proper combinations of one or more of these monomers, many polymer variations can be produced. These polymers, after properly mixing with plasticizers and stabilizers, are then used in hundreds of dif-

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ferent items. The three polymers, either individually or associated with each other, are relatively non-toxic.[1]

Seeler and associates studied the chronic toxicity of a copolymer of vinyl and vinylidene chloride.[2] This work was done because the copolymer was being considered for use as a constituent of a plastic film for wrapping food products. They reported that rats fed a diet containing 5% vinyl and vinylidene chloride copolymer for two years showed no toxic effects. Two dogs were fed a diet containing 5% vinyl and vinylidene chloride copolymer without evidence of toxic effects.

Some toxicological information also exists on the three monomers—vinyl chloride, vinylidene chloride, and vinyl acetate. Patty, Yant, and Waite[3] investigated the acute effects of vinyl chloride on experimental animals and found this to be essentially narcosis. Carpenter and associates,[4] in range finding studies, observed that a vapor concentration of 32,000 ppm of vinylidene chloride resulted in a portion of deaths of the six rats exposed for four hours. The vapor toxicity is reported to be of the same order as ethylene dichloride.[5] Carpenter and associates[4] also reported a level of 4,000 ppm of vinyl acetate produced some deaths under the same conditions.

B. Acrylonitrile—Butadiene Type

VARIOUS types of American made rubbers have been studied physiologically. Among those found to be acceptable for food use are Perbunan and Hycar (polymers of acrylonitrile and butadiene). However, the manufacture of these items does present some health problems.

Wilson and associates[6] reported on the toxicity of acrylonitrile in 1948. They stated that, in their observations, workmen handling cleaning operations in polymerizers with exposures varying from 16-100 ppm for 20 to 45 minutes frequently show symptoms of dull headache, fullness in the chest, irritation of all mucous membranes including the eyes, nose and throat, and a feeling of apprehension and nervous irritability. Some workmen complained of intolerable itching of the skin with no demonstrable dermatitis. Direct skin contact with acrylonitrile causes irritation and erythema followed by bleb formation, desquamation and slow healing. Wilson[7] reported several cases of acrylonitrile poisoning in which there developed mild jaundice, low grade anemia and leucocytosis. Given orally the minimal fatal dose of acrylonitrile in laboratory rats is stated[8] to be 150 mg/kilo body weight. Symptoms in these animals included respiratory changes, cyanosis, convulsions and death.

Because the mode of action of acrylonitrile in the human system appears to be similar to that of cyanide, the treatment of overexposure to acrylonitrile was outlined by Wilson and associates[6] to be the same as that for overexposure to cyanide. This treatment was proved to be life saving in several instances.

Vitamins B_1 and C have been found to be beneficial in preventing weight loss in laboratory animals exposed to acrylonitrile over long periods.

Wilson and associates[6] also suggested as a prophylaxis against overexposure to acrylonitrile that atmospheric concentrations should not exceed 20 ppm. This necessitates enclosure of processes to the maximum degree possible and the effective use of mechanical exhaust ventilation.

Skin contact should be avoided, not only because of the compound's vesicant action, but also because of possible toxic systemic effects. In the case of skin contact with the concentrated compound, immediate washing with copious quantities of soap and water is necessary. If spilled on clothing, the clothes should be immediately removed and a shower taken by the individual. The effect of chronic low-grade atmospheric or skin exposures on humans is still undetermined. It is, therefore, advisable that working personnel be given periodic physical examinations, with special emphasis on hematology and liver and kidney functions. The determination of the thiocyanate level in both blood and urine has been suggested as an index of overexposure.

Wilson and associates[6] also reported on the toxicology of butadiene. They stated that butadiene is practically innocuous, aside from its narcotizing and anesthetizing effect at very high concentrations. Human subjects who were exposed to 8,000 ppm of butadiene complained of eye irritation, blurring of vision, coughing, nasal congestion, and drowsiness.[9] Subsequent repeated exposures gave no indication of cumulative action.

A complete examination of the chest including an x-ray, blood examination and urinalysis were not informative. Subsequent follow-up examinations were also negative. In laboratory animals[9] subjected to high exposures of butadiene, irritation of all of the mucous membranes and respiratory tract occurs along with varying degrees of narcosis. Acute deaths are due to pulmonary edema. Delayed deaths are due to chemical pneumonia following pulmonary irritation. Experimentation with butadiene in laboratory animals indicates that butadiene is not a safe general anesthetic because there is not complete muscular relaxation even in the fourth stage. Death ensues rapidly when the laboratory animal is kept in deep anesthesia for any length of time.

Wilson and associates[6] stated that workmen anesthetized with or suffering from exposure to butadiene should recover completely, providing they are removed from exposure while respiration and heart action are still strong. Oxygen by inhalation should be administered until the pulse and blood pressure remain normal and the color is good. Symptomatic treatment is indicated.

Special precautions need to be observed in handling the compound from a fire and explosive standpoint. These include enclosure and mechanical exhaust ventilation and will in most cases automatically control the health hazard. There is no apparent systemic injury to humans in concentrations below 5,000 ppm. Any complaints which include eye and respiratory irritation, headache and vertigo might be considered as indicative of excessive exposure.

TABLE I.

COMMON PLASTICS	USES	PROPERTIES
Acrylics	Aircraft turrets, auto tail lights, brush backs, signs (Dynel, Acrilan, Orlon textiles).	Optical clarity, good weather resistance, wide color range, shatter resistance, machinability.
Alkyds and Rosin Modifications	Linoleum surfacings, paints for refrigerators and autos, ignition parts, magneto rotors.	Fast curing, good dimensional stability, good electrical insulation, good heat resistance.
Aminos (Urea and Melamine)	Buttons, dishes, laminated table tops, housings for kitchen appliances.	Unlimited color range, good electrical insulation, resistance to organic solvents.
Cellulose Plastic Materials	Display packaging, irrigation pipe, frames for eye-glasses (rayon and acetate textiles).	Toughness, high impact strength, ease of fabrication, lustrous finish, good electrical insulation.
Coumarone-Indene and Petroleum Resins	Asphalt floor tiles, aluminum paints, waterproof coatings, printing inks.	Resistance to water and caustic cleansers, compatibility with compounding ingredients, glass.
Epoxies	Printed circuit backing, adhesives, surface coatings, transformer and motor laminates.	Excellent adhesion, resistance to chemicals and heat, can be cured at room temperatures.
Fluorocarbons	Pump diaphragms, chemical tubing, high temperature insulation.	Extreme resistance to corrosive agents and solvents, wide temperature range, high impact strength.
Nylon	Gears, slide fasteners, combs, tumblers, tennis racket strings (nylon textile).	Good strength and toughness over wide temperature range, wear resistance, self-lubricating.
Phenolic and other Tar Acid Resins	Telephone handset, radio-TV cabinets, shell molding, dials, grinding wheels, plywood.	Hard and rigid, good temperature range, strong, good electrical insulation, low water absorption.
Polyethylene	Squeezable bottles, semi-rigid kitchenware, packaging, coaxial cables.	Inert to solvents, flexible and tough over wide temperature range, nontoxic, odorless, tasteless.
Polyester Resins	Reinforced plastics for auto bodies, boats, translucent panels (Dacron textiles).	Weather resistance, can be formed with low pressure, strong, colorful, compatible with many fillers.
Silicones	Insulation for generator coils, auto polishes, waterproof coatings, circuit breakers.	Extreme heat resistance, low water absorption, good dielectric properties over wide frequency range.
Styrene Resins	Kitchen housewares, refrigerator parts, toys and novelties, wall tiles, lighting fixtures.	Lightest of commercial plastics, excellent moldability, unlimited color range, tasteless, odorless.
Vinyl Resins	Floor tile, packaging film, rainwear, toys, upholstery material, pipe and pipe fittings, valves, electrical insulation, sponge, machine and structural parts, metal and fabric coatings.	Tough and strong, unlimited color range, excellent electrical insulation, resistance to chemicals, oil and weathering.

C. Miscellaneous Types

SOME of the newer synthetic resins which have been physiologically studied are the silicones, the polyethylene gylcols (carbowax compounds), and teflon (polytetrafluoroethylene). Rowe *et al*[10] found upon feeding guinea pigs for 50 days in amounts up to 3% of the daily diet no indication of toxicity with DC resins 993 and 2102. They also found that DC Pan Glaze possessed a very low order of oral toxicity when fed to the rat. Shaffer and Critchfield[11] concluded from their study of carbowax compounds 1,000, 1,540, 4,000 and 6,000 that no significant gastrointestinal absorption occurred when fed to rats. They also administered intravenously compounds 1,000 and 6,000 to humans and found they were readily excreted to a high degree.

Polytetrafluoroethylene (Teflon) is a synthetic resin with exceptional resistance to both heat and chemicals. It is being used for electrical insulation, for special types of tubing, for coating molds and bread pans, and for gasket materials in jet engines. Stokinger[12] has described the ill effects which may result when Teflon is heated to about 360° F as well as from exposure to the finely divided polymer itself. These effects resemble, in the case of the polymer, those of metal fume fever; in the case of the sublimate (resulting from heating the polymer) those of hydrogen fluoride poisoning. In using Teflon, adequate ven-

tilation is necessary to avoid ill effects. Lehman[1] reports that baking tests have shown no significant increase of the fluoride level of bread baking pans which have been coated with Teflon.

Plasticizers

LEHMAN in July, 1951,[1] stated that plasticizers presented more serious toxicological problems than the resins because there is always the possibility that these materials may be leached out by food substances. The plasticizers which have had adequate pharmacological study demonstrating their harmlessness in the amounts now used in finished commercial films are:

Ethyl Phthalyl ethyl glycollate.
p-tertiary Butyl phenyl salicylate.
3-(2-Xenoxyl)-1,2-epoxypropane.
2-Ethylhexyl diphenyl phosphate.
Butyl phthalyl butyl glycollate.
Glycerol monooleate.
Acetyl tributyl citrate.
Di-iso-butyl adipate.

Lehman classified as unsuitable for food use the following:

Dicyclohexyl phthalate.
Dibutyl phthalate.
Methyl phthalyl ethyl glycollate.
Di-iso-octyl phthalate.
Dioctyl adipate.
Dibutyl sebacate.
Dioctyl sebacate.
Dicapryl sebacate.

Seifter in 1943[13] made acute toxicity, chronic toxicity and skin irritation studies on dibutyl phthalate. His summary and conclusions were:

1. Dibutyl phthalate is a mild primary skin irritant for animals and humans.

2. Dibutyl phthalate taken by mouth is acutely toxic.

3. Dibutyl phthalate ingested daily over long periods of time in amounts up to 2.5 gm. per kilogram of diet, does not produce chronic poisoning.

Smith[14] studied dibutyl phthalate and found the acute lethal oral dose to be about 8 gm. per kilogram. When administered chronically in the diet the maximum concentration which did not significantly reduce normal growth was 0.25%. The feeding of dibutyl phthalate even in the highest dietary concentrations did not provoke specific gross or microscopic pathologic changes. His findings also suggested that dibutyl phthalate was metabolized in the body in much the same way as the fat normally ingested in the diet. He did not feel that it was safe to incorporate dibutyl phthalate in films for wrapping foods even if the calculated safety factor was in excess of 1400.

Seifter[13] in studying dicapryl phthalate made the following summary and conclusions:

1. Dicapryl phthalate is not a primary skin irritant for animals or humans.

2. When taken by mouth dicapryl phthalate has a low acute toxicity.

3. Ingested daily over long periods of time, in amounts up to 2.5 gm. per kilogram of diet, dicapryl phthalate does not produce chronic poisoning.

Seifter in 1943[13] came to the following conclusions concerning triethylene didecoate:

1. It is not a primary skin irritant for animals or humans.

2. When taken by mouth, it has a low acute toxicity.

3. Ingested daily over long periods of time in amounts up to 2.5 gm. per kilogram of diet, it does not produce chronic poisoning.

Smith[14] found that the acute lethal oral dose of butyl stearate was greater than 32 gm. per kilogram. When butyl stearate was administered chronically in the diet, the maximum concentration which did not significantly reduce normal growth was more than 6.25%. Butyl stearate in the highest dietary concentration did not provoke specific gross or microscopic pathologic change and in dietary concentrations of 6.25% had no adverse effect on fertility or the number of viable young in the litter. There was in this concentration slight retarded growth of the young. He felt that, based on the above data, butyl stearate when incorporated in films for wrapping food appeared to possess little, if any, potential hazard for humans, the calculated safety factor being in excess of 1,400.

Smith[14] came to the conclusion that the acute lethal oral dose of methoxyethyl oleate was approximately 16 gm. per kilogram and when administered chronically in the diet of rats the maximum concentration, which did not significantly reduce normal growth, was 0.01% to 0.05%. He found renal calculi in three of seven rats fed 1.25% methoxyethyl oleate for more than six months. He felt that methoxyethyl oleate was hydrolized by pancreatic lipases as rapidly as triolein. He did not feel that methoxyethyl oleate should be incorporated in films for wrapping food.

Smith[14] concluded that the acute lethal oral dose of dibutyl sebacate was between 16 and 32 gm. per kilogram and that when administered chronically in the diet of rats, the maximum concentration which did not significantly reduce normal growth was 6.25%, and that when fed in the highest dietary concentration, there were no specific gross or microscopic pathologic changes. Dibutyl sebacate in dietary concentrations of 6.25% had no adverse effect on fertility or the number of viable young in the litter. It did cause a slight retarded growth of the young. Smith felt that this plasticizer was metabolized in the body in much the same way as fat normally ingested in the diet, and that when it was incorporated in films for wrapping food appeared to possess little, if any, potential hazard for humans, the calculated safety factor being in excess of 1400. Mallette and Von Haam[15] state that dibutyl sebacate is a non-toxic plasticizer, with no irritating or sensitizing effect on the skin, and that dibutoxyethyl phthalate is a non-toxic plasticizer with no irritating or sensitizing effect on the skin.

Mallette and Von Haam[15] listed the following as non-toxic plasticizers:

Di-2-ethylhexyl adipate.
Dibutyl cellosolve azelate.

Cyclohexyl azelate.
2-ethylhexyl azelate.
Methyl isobutyl carbinol azelate.
Pentasol azelate.
Diethylene glycol dicaprate.
Dibutoxyethyl diglycol carbonate.
Octadecene nitrile.
Dibutoxyethyl phthalate.
Dicapryl phthalate.
Methylacetyl ricinoleate.
Dioctyl sebacate.
Dibutyl sebacate.
"Plasticizer 50 B" (Barrett).
"Plasticizer Ellicott H."
"Plasticizer SC" (Drew).
"Paraplex G-25" (Rohm & Haas).
"Paraplex G-40" (Rohm & Haas).
"Plastolein X-55" (Emery).

They stated that five of the plasticizers examined showed a moderately toxic effect in laboratory animals. They were dioctyl phthalate, butylbenzyl phthalate, "santicizer 140," "santicizer 141," and "flexol 8N8."

Di(2-ethyl hexyl) phthalate (commercially referred to as dioctyl phthalate, DOP, and 2-ethyl hexyl phthalate) was studied by Hodge[16] with respect to acute oral and intraperitoneal toxicity in rats and mice. He concluded that it had a very low order of toxicity. Shaffer, Carpenter and Smyth studied it in 1945.[17] Their conclusions were that it is a chemical of low toxicity and that the health hazards involved in its use as a plasticizer are slight. Such injurious action as it does exert within the body appears to be due to the alkyl part of the molecule rather than to the phthalate portion.

Mallette and Von Haam[15] found that dioctyl phthalate had a moderately toxic effect in laboratory animals and that the intraperitoneal injection of dioctyl phthalate proved fatal in doses higher than 2 gm. per kilogram of body weight. Lower doses produced weight loss, leucocytosis, severe anemia and hematuria from which the animals recovered after a month or two. No delayed effect or permanent injury was noted in the surviving animals. They also showed that dioctyl phthalate had a moderate skin irritating effect.

Carpenter, Weil and Smyth[18] reported the results of feeding Di(2-ethyl hexyl) phthalate for two years to rats and for one year to both dogs and guinea pigs. They obtained relatively uniform responses from all three species, with the two-year "no effect" level for rats falling between .06 and .20 gm. kilogram per day, and the one-year "no effect" level for both dogs and guinea pigs approximating .06 gm. per kilogram per day. Lehman[1] reports that food packaging films containing this compound as a plasticizer are satisfactory for wrapping foods with a high water content, but are unsatisfactory for use with foods having a high fat content, because of the ready solubility of the plasticizer in fats and oils. Halpern and Weiss[19] found no irritation or induced sensitivity when 200 humans were patch tested with vinyl film containing dioctyl phthalate as the plasticizer.

In 1952 Mallette and Von Haam[15] reported on other plasticizers, several of which they found to be moderately toxic to rats in acute exposures. These were:

1. Butylbenzyl phthalate was fatal in rats after intraperitoneal administration of doses higher than 1.8 gm. per kilogram of body weight. Oral administration of more than 4 gm. per kilogram of body weight proved equally fatal. The animals died after four to eight days, showing weight loss, apathy and leucocytosis. The histological examination of the organs revealed toxic splenitis and degenerative lesions of the central nervous system with congestive encephalopathy, myelin degeneration and glial proliferation.

2. "Santicizer 140" (monotolydiphenyl phosphate) proved fatal in intraperitoneal doses of higher than 1 gm. per kilogram of body weight. Oral doses up to 4 gm. were supported. Toxic animals became lethargic on the second or third day and a profuse diarrhea developed. They died with symptoms of paralysis. Autopsy showed a generalized capillary paralysis with severe edema and numerous hemorrhages in the brain.

3. "Santicizer 141" (2-ethyl hexyl diphenyl phosphate or mono octyl diphenyl phosphate) killed animals after intraperitoneal administration of doses higher than 2.4 gm., but oral administration of 4 gm. per kilogram of body weight was tolerated. With the intraperitoneal administration the animals became paralyzed and lethargic. Recovery from non-fatal lesions was delayed. The histopathological examination demonstrated a severe acute hemorrhagic encephalopathy with cerebral edema, ganglion cell degeneration and small hemorrhages. As delayed effects, focal gliosis and persistent foci of myelin degeneration could be observed. Large fatal doses also proved a powerful hemolytic agent with marked vascular hemolysis, hemoglobinuria, and hemosiderosis of the spleen.

4. "Flexol 8N8" (N,N-di-beta-(2-ethyl hexyl) ethyl 2-ethyl hexylamide) proved fatal in doses higher than 4 gm. per kilogram of body weight. The animals developed convulsions followed by paralysis. The histological examination of the brain gave the picture of toxic hemorrhagic encephalopathy with edema, swelling of ganglion cells and small hemorrhages.

Their conclusions were that these four plasticizers proved moderately toxic in doses from 0.6 to 2.4 gm. per kilogram of body weight. The toxic reaction was displayed by the erythrocytes, the blood capillaries and the central nervous system. They also found in their studies 17 plasticizers to be slight or moderate skin irritants. Three—"Flexol 8N8," "Paraplex G-25," and "Paraplex G-40"—proved to be severe skin irritants.

A moderate sensitizing effect on the skin was found by Mallette and Von Haam[15] to exist with diethylene glycol dicaprate, methylacetyl ricinoleate, "Paraplex G-25," "Paraplex G-40," and "Santicizer 140."

Seeler *et al*,[20] in their studies on the chronic toxicity of acetyl tributyl citrate came to the following conclusions:

1. Rats showed no toxic effect after eating diets containing 200 ppm, 2,000 ppm, and 20,000 ppm of acetyl tributyl citrate for two years.

2. Dogs were given a daily oral dose of 140 mg. of acetyl tributyl citrate for two years without evidence of toxic effect.

Seeler *et al*,[21] on making chronic toxicity studies of butyl phthalyl butyl glycollate came to the following conclusions:

1. Rats fed diets containing 200 ppm, 2,000 ppm, and 20,000 ppm of butyl phthalyl butyl glycollate for two years showed no toxic effect.

2. Dogs were given a daily oral dose of 140 mg. of butyl phthalyl butyl glycollate for two years without evidence of toxic effect.

The results of both acute and chronic oral feeding, as well as skin absorption and irritation with 2-ethylhexyl diphenyl phosphate (Santicizer 141) are given by Treon *et al.*[22] These investigators found the compound to be innocuous when administered orally to rabbits and rats in a single large dose. No effects, either irritative or systemic, were found as the result of keeping it in contact with the abraded skin of rabbits for seven to 24 hours. Rats fed for two years on a diet containing 1%, 0.125%, and 0.0625% by weight of the compound showed no pathology, but did show a retarded growth rate at the 1% level. Dogs fed the compound at dietary levels of 2.5% for two years showed retarded growth, but those fed a 1.5% level grew normally.

Treon, Cappel, and Sigmon have found[23] that a high percentage of Santicizer 141 is excreted in the feces of both rabbits and humans unchanged. Halpern and Weiss[19] have shown that films plasticized with Santicizer 141 are not irritating and do not induce sensitivity in humans.

Stabilizers

MANY different materials are being used as stabilizers for plastics. The specific type of plastic with particular reference to its use, governs to a large degree the stabilizer to be selected. Obviously, uses such as that of food packaging where there might be leaching of the stabilizer into the food require materials that are not harmful if ingested. Lehman[1] states that the following are not objectionable for food packaging:

Aluminum monostearate.
Calcium acetate.
Calcium ethyl acetoacetate acetate.
Calcium carbonate.
Calcium stearate.
Calcium glycerophosphate.
Mono- di- and tricalcium phosphate.
Calcium oleate.
Calcium ricinoleate.
Magnesium stearate.
Magnesium glycerophosphate.
Mon-, di-, and trimagnesium phosphate.
Disodium hydrogen phosphate.
Ammonium potassium phosphate.

Some of the most efficient stabilizers from the standpoint of performance, particularly for the vinyl resins, are the heavy metal salts of barium, strontium, lithium, cadmium, and lead. All of these compounds, however, possess a relatively high degree of toxicity and they are objectionable for use in items involving contact with human food.[1] There are, however, many plastic formulas for uses in products where toxicity is not of particular significance and consequently, one or more of these stabilizers can be safely used. Obviously, when these heavy metals are used, adequate, safe handling procedures must be utilized in the manufacturing plant. These involve the practice of good industrial medical and hygiene procedures.

Lehman[1] has also stated that zinc oxide, zinc stearate and salts of manganese and copper are not objectionable as stabilizers in food wrapping material if not more than 50 ppm of the metal leaches out into the food.

Some of the newer stabilizers for vinyl resins are the organic tin compounds. Elemental tin has been used for many years as a lining for food containers and is relatively harmless. The organic tin salts, however, while not known to be harmful have not thus far been shown to be sufficiently safe for use in food container applications. The plant manufacturing operations involving the use of the organic tin stabilizers may present some industrial health problems but again the degree or extent of these is not known at the present time.

Solvents

IN THE processing of plastics into products, a number of chemicals are used. These include aromatic hydrocarbons, chlorinated hydrocarbons, petroleum distillates, ketones, acetates and alcohols. These compounds are all toxic in varying degrees and present certain medical problems in their handling. Specific methods for determining the atmospheric concentrations of these chemicals can be found in Jacob's[24] text.

The American Conference of Governmental Hygienists[25] suggested the maximum allowable concentrations of many of the more common solvents in Table II.

The aromatic hydrocarbons are used extensively in the processing of plastics. Of these, benzene (benzol C_6H_6); toluene (toluol, $C_6H_5CH_3$); and xylene (xylol, $C_6H_4(CH_3)_2$) are the principal ones. These compounds are of value because of the fact that they are excellent solvents.

As pointed out by Wilson[26] benzol poisoning may result from absorption of benzene by either the respiratory tract, the alimentary tract, or probably the skin. Cases of poisoning in human beings have been found with exposures to atmospheric conditions as low as 25 ppm. Concentrations of 50 to 100 ppm are considered to be safe for the average person. Individual susceptibility varies. Acute benzol poisoning is rare.

As pointed out by Wilson[27] the pathologic manifestations of exposure to toluene are a matter of controversy. The conclusions reached by various authors are in decided variance with one another. Toluene poisoning is probably caused by absorption through the respiratory system, the skin, and the alimentary tract. The absorbed

TABLE II.
SUGGESTED MAXIMUM ALLOWABLE CONCENTRATIONS
(Parts per million parts of air)

Acetone	1000
Acrylonitrile	20
Amyl acetate	200
Amyl (iso) alcohol	100
Benzene (benzol)	35
Butadiene 1,3	1000
Butyl acetate	200
Butyl alcohol	100
Carbon tetrachloride	25
Ethyl acetate	400
Ethyl alcohol	1000
Ethylene dichloride	100
Gasoline	500
Heptane	500
Hexane	500
Propyl (iso) alcohol	400
Methyl alcohol	200
Methyl ethyl ketone	100
Naphtha (petroleum)	500
Perchlorethylene (tetrachlorethylene)	200
Propyl acetate	200
Stoddard solvent	500
Tetrachlorethane	5
Tetrachlorethylene	200
Toluene	200
Trichlorethylene	200
Xylene	200

vapors exert a progressive depressant action on the central nervous system and the bone marrow. Toluene is also a pronounced irritant to mucous membranes. A factor to be considered whenever it is employed is individual susceptibility. Exposure to concentrations of toluene from 200 to 500 ppm for six to eight hours will in most persons cause tiredness and lassitude. Concentrations over 500 ppm for one to three hours are definitely dangerous and will cause symptoms attributable to depression of the central nervous system and the bone marrow.

Xylene[6] is stated to possess more severe narcotic properties than benzene. Xylene poisoning is relatively uncommon because its volatility is lower than that of benzene or toluene. Chronic poisoning does occur. There is some evidence that xylene exerts an action on the blood forming organs similar to that of benzene. Cases of aplastic anemia have been attributed to xylene vapors. There have been some cases reported in German literature of leukopenia and thrombocytopenia with no reduction in red cells.

The commonly used chlorinated hydrocarbons in the plastic industry are:

Carbon tetrachloride (tetrachlormethane) CCl_4.

Ethylene dichloride (dichlorethane) $C_2H_4Cl_2$.

Tetrachlorethane (acetylene tetrachloride) $C_2H_2Cl_4$.

Trichlorethylene (ethylene trichloride) C_2HCl_3.

Perchlorethylene (tetrachlorethylene) C_2Cl_4.

The most toxic of the group is tetrachlorethane, having, according to Matruchot,[28] a comparative toxicity of 6.0. Carbon tetrachloride is listed by the same author as having a comparative toxicity of 2.6, trichlorethylene of 1.0, perchlorethylene of 1.4, and ethylene dichloride of 1.6. According to Davis[29] and the U.S. Public Health Service,[30] the maximum allowable concentration of carbon tetrachloride is 100 parts per million. According to Elkins[31] this level is too high and should be reduced to 50 parts per million.

Many of the petroleum distillates are used. Gasoline (unleaded), hexane, heptane, Stoddard solvent, varsol, and naphtha are mixtures of hydrocarbons, paraffins, olefins, cycloparaffins (naphthenes), aromatics, and other impurities including sulphur. Cracked gasoline may also carry a fairly high percentage of benzol. These substances are frequently referred to by the general name of benzine. This is to be distinguished from benzene (benzol). These distillates are narcotics, and it is possible to produce complete anesthesia with heavy doses. However, their anesthetic properties are much less than those of the aromatic and chlorinated hydrocarbons. For this reason they may be more desirable for commercial use. Drinker and associates, in studying the effects of gasoline vapors[32] found that concentrations from 270 to 500 ppm were tolerable. Neuromuscular symptoms began at about 900 ppm; mild intoxication at 2,000 ppm.

Acetone, methyl ethyl ketone, methyl isobutyl ketone, and methyl amyl ketone are also used. In our experience no cases of occupational disease have been attributed to the ketones.

Methyl, ethyl, propyl, isopropyl, butyl and isoamyl acetate may be used. These solvents are not considered severely toxic and in most cases the allowable concentrations are based more on comfort than on toxic requirements.

Methyl, ethyl, isopropyl, amyl and butyl alcohol are all used at times in plastics manufacture. Methyl alcohol is a source of grave injury to many industrial workers. It has a specific action on the optic nerve, and with long enough exposure, blindness may result. The action is that of inflammation of the optic nerve followed by atrophy. A considerable amount of methyl alcohol poisoning was noted during prohibition days when wood alcohol was used in large amounts with subsequent optic nerve degeneration and blindness. The other alcohols, because of their volatility are not considered to be especially dangerous. Cases of narcotic poisoning have been attributed to them but not proved. The higher alcohols, like butyl and amyl, have in addition an irritant action as well as some poisonous action on the protoplasm.

Summary

THE ADVENT of a great industry for the manufacture of articles of all kinds made from various chemical compounds has created many new problems for the industrial physician and the industrial hygienist. Many of the compounds used are new and very little, if anything, is known about their toxicity. Also, since there are no set formulas or recipes, each plastic article may have a different composition.

This paper attempts to discuss the toxicity of the more common compounds now being used in

plastics manufacture. Resins, plasticizers, stabilizers and solvents are discussed in some detail in regard to their toxic properties. The scarcity of knowledge of the properties of many of the chemicals is sufficient reason for further study.

It is not enough for industry to make better things cheaper; it must also make them safely.

Resume

ARTICLES made of a variety of chemical combinations commonly called plastics have found increasing favor with the consuming public. Many useful products can be made stronger, better looking, longer wearing and at lower costs employing these versatile new materials. The imaginative creativeness of the human mind is evident in our new world of plastics. To create these man-made marvels, the research chemists and development engineers have not only used known chemicals but also have created new ones.

Unfortunately, many of the chemicals currently used are known to be highly toxic. Even worse, the toxicity of many of the newer chemicals is not even known. Thus, industrial medicine and hygiene face serious problems both from known and potential toxic hazards. Considerable information has been published concerning some of the chemicals now being used in plastic manufacture, and at the present time many chemicals are undergoing toxicological investigation.

The authors of this paper have accumulated information on many of the resins, plasticizers, stabilizers and solvents being used in the manufacture of numerous plastic articles. It will be noted that the information is meager in some instances while in others it is quite complete, but, to our knowledge, this comprehensive summary on the toxicology of plastics has not heretofore been attempted.

Among the authors' conclusions is that industry must maintain strong Departments of Industrial Medicine and Hygiene to control toxicological hazards. Many industries are diversifying manufacturing activities and entering fields of endeavor for which previous experiences may not have prepared them. Highly toxic chemicals cannot be successfully handled in a haphazard manner and it is essential to invest money for toxicological investigation, because to be without such programs is foolhardy and more expensive in the long run. No industry can afford to endanger the health of its people by knowingly exposing them to toxic materials.

It is not enough for research chemists to discover a chemical combination, which will create a new sales masterpiece. The industrial hygienist must also determine the toxicity of the chemicals involved and designate ways and means of handling them safely. If the sales potential of a new plastic does not warrant toxicological study, then the product should not be produced.

Another conclusion of the authors is that much additional toxicological study is necessary on plastics, and it is hoped that the toxicology of plastics can be added to and made more complete, year after year.

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