Plastics

The Toxicology of Synthetic Resins

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This presentation is the third revision of a paper originally written [1] in 1954. It represents a compilation of the literature concerning the toxicological properties of synthetic resins. While not all-inclusive, the bibliography can be used as a reference for the investigator of the toxicology of plastics. The second revision [2] was presented in November, 1955.

Plastics is a familiar word to everyone. Who among us does not possess or use something made from a plastic? The manufacture of plastic articles and materials is both big and little industry. A small shop with few employees can make profitably a plastic water pistol. A large company makes nylon stockings or plastic garden hose. Automobile bodies and telephones are molded from plastics. These plastic articles are important to our social progress, and the jobs resulting from their manufacture are important to our national economy.

Plastic compounds are ever changing. The public demand for articles made from plastics is so great that the growth possibilities are seemingly endless. Vast sums of money are spent each year on plastic research, resulting in new materials. The industrial physician and hygienist must know the toxic properties of these items. The working environment is only as safe as the industrial hygienist makes it. Any material can be handled safely if one knows what it is and then handles it properly. Overexposure to a toxic material represents carelessness or ignorance.

Received for publication Nov. 18, 1959.

The B. F. Goodrich Co.

Presented at the Industrial Health Conference, Chicago, April 30, 1959.

Numerous papers have been written by authors from many different parts of the world concerning the general hazards of the plastic industry.[3-8] Obviously, occupational hazards may exist in the production and processing of some plastic material.[9] Toxic hazards can arise from the use of plastics which contain toxic substances, particularly in food-packaging applications where extraction into the food may occur. Polymerized synthetic resins, which form the base for many plastics, in themselves are usually not a hazard because of their insolubility and unreactivity. The risk arises from plasticizers, lubricants, stabilizers, colors, and fillers used with them to form the finished plastic.[10] There may also be significant hazards existing in the use or manufacture of the monomers of these resins, prior to polymerization.

In this discussion we have separated the resins into general classifications. In so doing we appreciate that there is considerable overlapping in many instances.

I. Acrylic Resins

The acrylic resins are used in many different ways including the making of aircraft turrets, automobile tail lights, brushbacks, signs, and various types of textiles. Nonirritating contact lenses for the eye can be made from methyl methacrylate.[11] These resins are extensively used in maxillofacial surgery. Prosthetic appliances for various parts of the human body can be fashioned from acrylic plastic material. An acrylic plastic material is used as a replacement [12] for blood vessels and heart valves because it does not promote the clotting of blood.

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acrylic resins have the best properties of all of the synthetic resins for use in facial surgery and produce minimum tissue reactions. They feel that the acrylics are better than any other previous material for tissue compatibility [17] and that they can be used in cosmetic surgery without causing skin irritation. Human implants have been made.[18] Intraocular acrylic lenses have been used as a substitute for the lenses of the eye for three and one-half years and over 150 successful eye operations have been reported without evidence of excessive foreign-body reaction.[18]

The use of an acrylic plastic replacement for the femoral bone head has shown a high percentage of failure due to sepsis.[18] However, the septic process is not from direct irritation by the acrylic material. The production of malignant tumors in rats by the implanting of plastics of various types has been reported,[19,20] but there are no reported cases of malignant growths developing in human beings from their use.

Laskin [21] referred to an experiment in which subcutaneous implantation of acrylic film in mice results in a 25% incidence of fibrosarcomas. These tumors developed between 257 and 469 days after implantation. Because of these findings he cautioned further use of acrylic in humans for purposes of femoral heads, intraocular prostheses, and jaw reconstruction.

MacKay [21] referred to the use of methyl methacrylate implants for the repair of cranial defects. In over 100 cases he cited no significant reaction to the substance even when it was placed in infected wounds. He considered the plastic "biologically entirely inert and innocuous."

Morgenstern and associate [22] described a case of sensitization to methacrylic acid and its polymerization products resulting from their use in dental prosthesis.

Patty [23] stated that polymerized methyl methacrylate is inert; only its stabilizers and antioxidants have adverse physiological effects, particularly dermatitis. Because of its inert properties, it was chosen to make an artificial kidney.

Karpov [24-26] reported on the effects of monomeric methyl methacrylate vapors. Symptoms of irritability, tiredness, somnolence, headache, loss of appetite, and a drop in blood pressure—attributed to a disturbance of the dynamic equilibrum in the cortex of the brain caused by inhalation of these vapors—were observed. In human beings it lowers the blood pressure.

Deichman [27] and Spealman [28] have studied the effects of monomeric methyl methacrylate vapors on laboratory animals. Deichman found that a concentration of 19 mg. per liter of air killed all exposed animals in 2.5 to 5 hours. Gross pathological changes were confined to the respiratory system. Spealman observed that the vapors were more acutely toxic than acetone for mice and less than those of ethyl acetate. An LC_{50} for mice for three hours' exposure was found to be 55 mg. per liter.

Karpov [25] gave a suggested tolerance for monomeric methyl methacrylate vapors in industrial establishments of 0.05 mg. per liter. He also observed that the respiratory mucosa may be irritated when vapor concentration reaches 0.25 mg. per liter.

Raines [29] called attention to the high toxicity of methyl methacrylate, widely used as a monomer in the polymerization of plastics and dentures. Upper limits of its vapor concentration in air which are permissible are stated as 0.05 mg. per liter.

Summary.—Methyl methacrylate vapors have some systemic effects on the brain cortex and on the blood pressure, resulting in lowering. The acrylic resins themselves appear to be substances which can be used successfully as bone replacements, artificial eyes, and other prosthetic appliances. When placed in certain regions of the human body, however, they should be kept under observation because tumor formation, tissue reaction, and sepsis have been reported.

II. Alkyd Resins

The alkyd resins are being used in the manufacture of linoleum surfacings, paints

for refrigerators and autos, ignition parts, magnetorotors, and food wrappings.

Morris,[30] on reviewing the reactions involved in the production of aminoplasts, phenoplasts, and alkyd resins, stated that the finished products are dermatologically inert.

Schwartz, Tulipan, and Birmingham[31] found that the alkyd resins may produce dermatitis. Schwartz[32] reported that alkyd resins when used as finishes for textiles have caused some cases of dermatitis.

Summary.—The alkyd resins are capable of causing occasional mild cases of dematitis.

III. Amino (Urea and Melamine) Resins

This group of plastics is used for many articles including buttons, dishes, laminated table tops, and housings for kitchen appliances. They are used as soap fillers and finishes for textiles. They can be used to treat paper for food-wrapping purposes.

Elkins[33] stated, "nitrogen bearing plastics, such as melamine, have been said to give off hydrogen cyanide when heated, but the quantities are apparently not sufficient to produce real danger."

Hodgins[34] stated that heat-converted films of urea-formaldehyde-ethylene glycol resins used as food-wrapping material showed no toxic effect when fed to guinea pigs in single doses of 100 mg. Repeat doses to rats of 10 mg. per day for 30 days produced mild effects on the liver, kidney, and gastrointestinal tract. Moss,[35] in studying the pyrolysis of melamine formaldehyde compounds, found that mixtures of 200 ppm carbon monoxide and 10 ppm hydrogen cyanide were produced which killed rats within 30 minutes. He noted that hydrogen cyanide increases the rate of respiration and, hence, intake of carbon monoxide. Schneider[36] studied the effects on human skin of soaps containing urea-formaldehyde resin filler. No significant difference was observed between soaps filled with urea-formaldehyde and other soaps. Cases of dermatitis were found due to the fatty acids used.

Segal[37,38] found little indication of toxicity in rats fed Amberlite resin, a polyamine formaldehyde resin, when diets containing 0.5% to 2% of the crude resin were used. There was no histological evidence of damage resulting from ingestion of the resins noted. He stated that the over-all toxicity of Amberlite, even at 20%, is negligible.

Markuson[39] reported on the prevention and control of dermatitis due to formaldehyde resins.

Vil'kovich[40] noted that the introduction of powdered aminoplastic resin, used in kitchenware, into the regular diet of white mice led to 70% to 80% fatalities. He also found both hot and cold aqueous extracts, obtained by placing water into aminoplastic dishes, led to considerable intoxication.

Schwartz[31,32] felt that urea-formaldehyde resins, when used as finishes for textiles, caused occasional cases of dermatitis.

Lehman[41] stated that a polymer of urea-formaldehyde is acceptable as a treatment of paper for food-wrapping purposes. He also stated that melamine formaldehyde polymer is satisfactory for the same purpose.

Lieber,[5] in discussing industrial dermatitis, stated that the amino resins can affect many people who have hereditary hypersensitivities.

Summary.—The amino resins (urea and melamine) can in certain combinations, particularly melamine formaldehyde compounds, pyrolyze into hydrogen cyanide and carbon monoxide. Urea-formaldehyde-ethylene glycol resins can safely be used as food-wrapping material. The aminoplasts may be very toxic. Dermatitis has resulted in workers handling these resins.

IV. Cellulose Plastic Materials

Cellulose plastic materials are used extensively in display packaging, irrigation pipe, frames for eyeglasses, cigarette filters, tire cord, and in rayon acetate textiles. Some of the cellulose plastics are suitable for food packaging.[42]

Maramorosch[43] stated that sheets of cellulose acetate were found to be toxic to plants and fish. This toxicity is due to diethyl phthalate.

Oppenheimer [19,20] noted that malignant tumors including sarcomas were produced in groups of rats and mice by subcutaneously imbedding cellophane films. He stated that additives, plasticizers, etc., apparently do not account for the production of these malignant tumors.

Schwartz, Tulipan, and Birmingham [31] found only rare cases of dermatitis due to cellulose resins.

Parmeggiani and associates,[9] in discussing the occupational risks and pathology in the production and manipulation of some plastic materials, stated that in the manufacture of cellulose acetate, the acetic acid content in the air caused mucosal irritation, blackening of the skin, and erosion of the teeth.

Summary.—Cellulose plastics can be used safely externally. They only rarely produce dermatitis. Internal use may be hazardous. There is some occupational risks in the manufacture of cellulose acetate.

V. Coumarone-Indene Resins

Coumarone-indene resins are used in the manufacture of asphalt floor tiles, aluminum paints, waterproof coatings, printing inks, and chewing gum.

Geiger [44] stated that coumarone-indene resins present little if any industrial hazard from the point of view of toxicity, as witnessed by their long-continued use in chewing gum. The main hazards are involved in the use of the monomers, to which some individuals exhibit allergic tendencies.

Cases of dermatitis among workers handling coumarone-indene resins [31] have been reported.

Summary.—A relatively nontoxic variety of resins. The hypersensitive person can acquire a dermatitis from handling these materials.

VI. Epoxies

During the past few years there have been marked advances made in the chemical technology of the epoxy resins. Currently these resins are widely manufactured and are available under a variety of trade names. They are used in corrosion-resistant surface coatings, molding compounds, castings, laminating or reinforcing plastics, encapsulating electronic circuits, printed circuit backing, and adhesives. Metal-to-metal bonding can be accomplished with an epoxy adhesive.

Lea and associates [45] have attempted to assess in a general manner the irritating and sensitizing capacity of the component materials in the epoxy resin formulations. The resins were found to be irritating to the skin by means of human patch-testing.

Hine and associates [46] discussed the toxicity of six epoxy resins.

Morris [47] stated that exposure to epoxy resins in industry has resulted in dermatoses. He said that the epoxies, the curing agents, and some of the additives are severe skin irritants.

Bourne [48] stated that contact with triethylenetetramine used as a polymerizing agent will give rise to an erythema of the face and arms.

Dorman [49] stated that uncured liquid epoxy resins and amine type curing agents are capable of causing allergic epidermal eczema. He outlined preventive measures that can be undertaken.

Grandjean [50] stated that dermatoses occurred in half the workers using an epoxy resin in 11 factories making electrical equipment.

Pitt and Paul [51] stated that a series of *N*-hydroxy alkyl-polyamines were evaluated as cross linking agents for polyepoxy resins. The availability of these cross linking agents with lower toxicity offers a means of overcoming one of the major deterrents in the widespread utilization of epoxy resins.

Summary.—The epoxy resins are relatively inert chemically and are resistant to heat. Severe skin irritation can occur in their manufacture and use. They must be handled with care. The curing agents used with these resins appear to be the primary cause of the skin irritant effects.

VII. Fluorocarbons

The fluorocarbons are used in the manufacture of such articles as pump diaphragms, chemical tubing, high temperature insulation, coating of molds and bread pans, and gasket material in jet engines. Teflon is being used extensively in surgery for sutures and tubing.

Recent work by Zapp and associates [52] indicates various fluorine compounds to be present in the decomposition products, the specific ones, as well as the amounts of each, depending on the temperature of decomposition. In the range of 300 to 360 C, hexafluorethane was observed; above 380 C, an extremely toxic compound, octafluoroisobutylene, was detected; from 500 to 550 C, the chief pyrolysis products were tetrafluoroethylene, hexafluoropropylene, octafluorocyclobutane, octafluoroisobutylene, a C_5 olefin, and a complex mixture of perfluoroolefins.

Fairhall [53] stated that polytetrafluoroethylene (Teflon) is physiologically inert and has been rated as nontoxic. However, when heated above 400 C, unidentified volatile gases are evolved which may be toxic. Inhalation of Teflon dust appears to produce a condition resembling metal-fume fever. Pulmonary edema may result.

Stokinger [54] stated that industrial hazards from Teflon are due to exposure to its dust and to its decomposition products derived from heating. In the first instance, a condition resembling metal-fume fever, "the shakes," is observed. The effect usually disappears within 24 hours with no after-effect. There is pain and aching in muscles and joints, accompanied by chills and profuse perspiration alternating with fever. When heated above 360 F, the Teflon sublimate is believed to contain absorbed hydrogen fluoride. This can produce irritation of nasal membranes and may ultimately result in pulmonary edema.

Wilson and McCormick [1] stressed the need for adequate ventilation when using Teflon to avoid ill effects.

LaVeen,[55] in reporting on the tissue reaction to plastics used in surgery, made special reference to Teflon. He felt that it could be safely used. However, Oppenheimer [19] noted that malignant tumors have been induced by Teflon when it was imbedded in rodents.

Treon and associates [114] reported animal fatalities resulting from exposure to the decomposition products of Teflon and Kel-F when heated to 752 F.

Lehman [42] found that polytetrafluoroethylene, when used as a coating for bread pans, created no significant increase in the fluoride level of the bread.

Sendroy,[56] in studying the effects of pyrolyzed products of PTFE (a fluorocarbon polymer) when used on electric motor windings, under conditions simulating those on submarine operations, concluded that no carbon monoxide hazard would exist with operating conditions in excess of 250 C but that excessive concentrations of fluorine compounds might arise.

Summary.—The fluorocarbons are extremely resistant to corrosive agents and solvents. The end-products are inert and nontoxic, but toxic decomposition products may be produced. Inhalation of Teflon dust may cause an effect resembling "metal-fume fever." Irritation of the mucous membranes and pulmonary edema can occur from inhaling the decomposition products.

VIII. Nylon

Nylon is used extensively in the manufacture of gears, slide fasteners, combs, tumblers, tire cord, tennis racket strings, and textiles. It is used as surgical suture material, catheters, and toothbrush bristles.

Experiments [57] have proved that the type of nylon polymer used in yarns is not toxic and does not cause any skin reaction. Nylon has met the rigid suture requirements of the medical profession.

Gipstein [58] reported that a papulovesicular dermatitis was observed on a 20-year-old woman and found that patch tests revealed that the nylon fabric, dyed or undyed, was the agent.

Inderfurth [59] stated that undyed and unfinished nylon possessed no toxicological property and caused no skin reaction. Its use as suture material and toothbrush bristles confirms this report.

Last [60] noted no intra-arterial toxicity from nylon catheters, and Schweisheimer [61] stated that nylon was well tolerated and applicable for bone sutures.

Nylon button type closures [12] are safely used for openings between the two auricles of the heart. Also surgical tubing has been made of nylon and has been used perfectly safely.

Blunt [17] noted that nylon, when studied for tissue inertness in dogs for periods up to six months, showed less reaction than silk or cotton. There was a small foreign-protein reaction about the implant after six months.

Oppenheimer [19] noted that some malignant tumors have been induced from imbedding nylon in rodents.

Summary.—Nylon is a perfectly safe material. The fashionable women of the world have proved this by wearing nylon hose. In spite of its widespread use, only occasional cases of proved contact dermatitis have been reported. Nylon can be implanted in the human body with little or no tissue reaction.

IX. Phenolic Resins

The phenolic resins are used in the manufacture of telephone handsets, electrical insulation, radio-TV cabinets, varnish, shell molding, dials, grinding wheels, plywood, surgical braces, and other external surgical prosthetic devices.

Demole [62] studied the effect of phenol-formaldehyde resins on gastric juice. The action on gastric acidity was variable and of short duration, and there was no influence on the proteolytic enzymes.

Elkins [63] reported that phenol-formaldehyde varnishes have been particularly bad producers of dermatitis.

Vedorov [64] made a clinical study of the sensitization and development of allergy in chemical workers exposed to various substances including phenol-aldehyde resins.

Luvoni [65] reported that several foundry workers handling phenolic-cresolic resins developed an eczematous dermatitis. Removal of the affected persons from exposure resulted in the disappearance of the skin affections. He felt that a form of allergy was responsible.

Sendroy [56] stated that electric motors insulated with CNSV, a phenolic resin, when operated continuously for 96 hours under conditions simulating submarine operation, gave off carbon monoxide in concentrations up to 1,620 ppm.

Phenolic laminates [12] have been safely used for braces and other external prosthetic devices.

Fairhall [66] stated that dermatitis may result from repeated or prolonged contact with low concentrations of phenol in any form. It causes about 20% of the dermatitis cases of the phenol-formaldehyde industry.

Lieber [5] believed that phenolic resins may affect many people who have hereditary hypersensitivity.

Summary.—The phenolics as finished laminates are inert and nontoxic. They can be used safely as external prosthetic appliances. Many workers exposed to these resins during manufacturing processes have developed severe dermatoses.

X. Polyethylene

Polyethylene plastic is used in the manufacture of squeezable bottles, semirigid kitchenware, packaging materials, coaxial cables, surgical tubing, cartilage and bone substitutes, and surgical repair materials.

Polyethylene [12] is used safely in surgical repair, suture tubing, skull covering, plastic lung prosthesis, arterial reinforcement, and hernial repair. Polyethylene has been used extensively as surgical repair materials, both in and out of the body, with no apparent adverse effects. Occasional skin reactions have been reported. In general, it appears to be a perfectly safe, nontoxic, inert mate-

rial. It does not change composition when it is autoclaved.

Patty [67] stated that polyethylene is inert and that only its antioxidants and stabilizers have adverse effects.

Lehman [42] found polyethylene to be satisfactory as a food-packaging material.

Bing [68] stated that physical rather than chemical characteristics influence the body reaction to polyethylene. Implantation of irregular pieces causes more reaction. Polyethylene mesh and nylon suture materials produce similar reactions. Macrophages are found to absorb a plastic sponge of formalized polyvinyl alcohol formerly thought useful as a permanent prosthesis.

Tusing [69] found no skin reactions and no evidence of systemic toxicity in rabbits after prolonged dermal contact with polyglycols.

Because it has no adverse effect on body tissue [70] and is not affected by normal temperature ranges, polyethylene is a satisfactory substitute for human cartilage and bone.

Tuell [71] stated that prolonged intravenous use of polyethylene tubing sometimes causes thrombophlebitis in the vein containing the tube. Tissue reactions are stated to arise from dicetyl phosphate in the mix or from the breakdown products of polyethylene which have been extruded at 250 C.

Oppenheimer [19,20] found that malignant tumors including sarcomas were produced in groups of rats and mice by subcutaneous imbedding of polyethylene.

Summary.—Polyethylene is a perfectly safe, nontoxic, inert material. It can be used as a surgical repair material both in and out of the body. Occasional tissue reaction can occur, probably only in the sensitive person.

XI. Polyester Resins

The polyester resins are used in the manufacture of reinforced plastics for automobile bodies, boats, and translucent panels, and in Dacron textiles. They are excellent for the formation of artificial limbs.

They are weather-resistant, can be formed with low pressure, are strong and colorful, and are compatible with many fillers. Very little has been reported concerning their relative toxicity. The end-products containing polyester resins are considered to be inert and nontoxic. Some of the organic peroxides used in their manufacture present safety and dermatology problems.

Polyester resins and glass cloth are used to form artificial limbs of light weight and great strength. Virtually no one seems to be allergic to this material.[72]

Lieber [5] said polyester resins may have a dermatitis effect in people who have hereditary hypersensitivity.

Summary.—The polyester resins are relatively inert, nontoxic materials. Virtually no one appears to be allergic to them.

XII. Silicones

The silicones are used for insulation for generator coils, auto polishes, waterproof coatings, silicone rubber, and circuit breakers. They are used in the medical field [73] in needles, syringes, tubing, and in ointment bases.

It is reported that silicones [74] in protective creams, suntan lotions, and other pharmaceutical preparations are nonsensitizing and nonirritating.

Schoog [75] found no evidence of silicone causing skin irritation and felt that it was safe to use it as an ointment base.

Lesser [73] stated that silicone fluids are practically inert physiologically and appear to be nontoxic. They have little or no effect when administered up to 2% of body weight. Certain silicone fluids cause a transitory conjunctival irritation in the eye but no corneal damage. Silicone-containing foods fed to rats showed a low order of toxicity. In skin tests silicone showed no irritation. Silicones used in the medical field in needles, syringes, taping, etc., are chemically inert and have no effect on blood samples taken for hematologic, bacteriologic, or biochemical study.

Taylor [76] reviewed the properties and their effects of the silicates and silicones.

Walker [77] studied the toxicity of silicone insulation in submarines.

Cutting [78] noted that DC 200 silicone produced renal tubular damage when fed as 1% of the diet of rabbits for three to four months. DC Antifoam A caused widespread cellular infiltration in the kidneys and the liver when fed as 0.25% to 1% of the diet for the same period.

MacDougall [79] reported that silicone rubbers appeared to be nontoxic when used in tissue culture techniques. This was in contrast to results with vulcanized rubber.

Poleman [80] noted no acute or chronic toxic effects of methyl polysiloxane, antifoam silicone emulsion, and the resin used for coating capsules.

Rowe [81,82] studied methyl silicones, methyl phenylsilicones, and methyl polysiloxane and found them to be relatively nontoxic. He reported that DC Antifoam A is very low in chronic oral toxicity but did cause transitory conjunctival irritation but no corneal damage.

Lehman [41,42] found methyl polysiloxane satisfactory for treating paper for food-packaging applications.

Coppack [83] reviewed the toxicological problems of silicones and plastics associated with organic chemicals in food processing.

Oppenheimer [19] noted malignant tumors were induced from imbedding silastic (silicone) in rodents.

Summary.—The silicones are practically physiologically inert and nontoxic. They may cause a transitory conjunctival irritation when introduced into the eye but no corneal damage. Silicones are nonsensitizing and nonirritating.

XIII. Polystyrene

Polystyrene resins are used in the manufacture of kitchen housewares, refrigerator parts, food packaging, toys and novelties, wall tiles, and light fixtures.

Goggin [84] stated that polystyrene is nontoxic and in molded form has no taste or odor.

Lehman [42] approved of the use of polystyrene as a food-packaging material.

Patty [85] stated that polystyrene is inert; however, the antioxidants and stabilizers may cause dermatitis.

Struthers [86] reported that polystyrene may be used in contact with the skin and food without danger. Polystyrene, free from low molecular weight polymer or addition agents, presents no health hazard from oral ingestion.

Oppenheimer [19] reported that malignant tumors have resulted from imbedding polystyrene in rats.

Lieber [5] stated that polystyrene resins may have a dermatitis effect in many people who have hereditary hypersensitivity.

Parmeggiani and associates [9] stated that nervous excitation, leukopenia, and occasional dermatitis followed exposure to ethylbenzene among polystyrene workers.

Summary.—Polystyrene presents no health hazard from oral ingestion or skin contact, being inert and nontoxic. In its manufacture some hazards are encountered, especially from ethylbenzene. Dermatitis can occur.

XIV. Vinyl Resins

The vinyl resins are used in the manufacture of floor tiling, packaging film, rainwear, toys, upholstery material, pipe and pipe fitting, valves, electrical insulation, sponge, machine and structural parts, and metal and fabric coatings. They are used for plastic blood-transfusion equipment and anatomical repair film.

Plastic blood-transfusion equipment [87] made of vinyl with nylon and phenolic molded parts has no toxic properties.

According to Lehman,[42] several of the vinyl resins have been found to be satisfactory for food-packaging materials.

Morris [88] studied the dermatological and chemical aspects of the vinyl plastics. Patty [89] stated that vinyl chloride and vinyl acetate plastics have proved to be inert; only their antioxidants and stabilizers have adverse physiological effects.

Pulaski [90] noted no signs of toxicity when large amounts, even up to 20 liters, of polyvinyl pyrrolidone had been given to human subjects. There is some storage of polyvinyl pyrrolidone in the tissues. He also stated that a decision as to the presence of chronic toxicity has not been determined as yet.

Armstrong [91] stated that dextran and polyvinyl pyrrolidone are much superior to saline in the maintenance of blood volume after venisection. Systemic allergic reactions occurred in some subjects who received dextran but in none who received polyvinyl pyrrolidone.

Bernhard [92] stated that polyvinyl pyrrolidone is not toxic, antigenic, pyrogenic, or infectious.

Lesser [93] stated that polyvinyl pyrrolidone is nontoxic by oral administration, skin absorption, inhalation, or injection. Studies made on its storage in the body do not show any toxic effects.

However, Hueper [94] has reported polyvinyl pyrrolidone to be carcinogenic to rats, and Lusky and Nelson [95] produced fibrosarcoma in rats with multiple subcutaneous injections.

Wilson and McCormick [1] reported no signs of toxicity in a chronic study of a vinyl-vinylidene chloride copolymer with which rats were fed for two years and dogs for one year at a 5% dietary level. Geon polyvinyl chloride [96] was found least toxic in a series of experiments on resins for use in the chest cavity. Vinyl copolymers and polyvinyl alcohols are reported under study for anatomical repair purposes.

Oppenheimer [19,20] did note that some malignant tumors resulted from imbedding polyvinyl chloride film in rodents.

Hedri and associates [97] stated that polyvinyl chloride V-10 is considered unsuitable for use in surgery due to toxic effects in the liver, kidney, and spleen of dogs and mice. These effects appear to be related to high monomer content and lead contamination of the V-10.

Roubal and Pokorny [98] stated that acne on the face and forearms of workers handling polyvinyl chloride sheets or products is caused by chlorinated naphthalene. Addition of paraffin to prevent adhesion facilitates the rise of this chemical to the surface and should be avoided.

Tuell [71] stated that polyvinyl chloride does not change chemical composition upon autoclaving.

Parmeggiani [9] stated that in the manufacture of polyvinyl chloride only slight signs of irritation existed.

Summary.—The vinyl resins are used for a variety of purposes. Polyvinyl pyrrolidone (PVP) is nontoxic and can be used in the human body. Polyvinyl chloride (PVC) has been stored with little reaction in the chest cavity. Some slight skin irritations have been observed in workers manufacturing PVC.

XV. Polyurethanes

This class of polymers is relatively new, having been commercialized in the United States primarily during the past decade. They are high molecular weight polymers and may be used in the manufacture of adhesives, plastics, rigid or elastic foams, or synthetic rubber.

Finished polymers are rather inert chemically and no more hazardous than more common plastics or rubbers.

The polymers are manufactured from a class of materials called diisocyanates. These materials present serious inhalation hazards. Common raw materials are toluene diisocyanate (TDI), methylene bis (4-phenyl isocyanate) (MDI), and para phenylene diisocyanate (PPDI).

In general, all the diisocyanates so far investigated show similar toxicological properties. Animal experimentation and limited human experience indicate that this type of chemical is extremely hazardous via inhalation. In acute inhalation studies on TDI, Zapp [99] found that 600 ppm for six hours was lethal to rats, while 60 ppm was not. Animals which died showed acute pulmonary congestion and edema. Six exposures, averaging 9 ppm, killed three of six rats.

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Thirty six-hour exposures of 1 to 2 ppm caused microscopic evidence of tracheobronchitis. Zapp concluded that TDI is a rather powerful irritant to the eyes, skin, and respiratory tract. Chronic exposures to 1 to 2 ppm of TDI resulted in bronchitis in experimental animals with the attendant hazard of bronchial pneumonia.

Zapp [100] stated that, although polyisocyanate polymers are physiologically inert, the monomers may cause irritation to the skin, eyes, and respiratory tract and allergic reactions. Polyurethane foam plastics caused virtually no skin irritation or sensitization. Pyrolysis products show some toxicity but are not more hazardous than those of other elastomers tested.

Industrial use of TDI has caused many cases of asthmatic type reactions, some very serious.

The high inhalation toxicity is reflected in the fact that the threshold limit value for TDI is 0.1 ppm.[101]

It is interesting to note that the odor threshold of TDI is about 0.4 ppm, and this means that odor cannot serve as a warning of hazardous concentrations.

Summary.—The polyurethanes are a relatively new class of polymers. The finished polymers are inert chemically and present no toxic hazards.

During manufacture severe industrial health hazards occur because of the use of isocyanates. These compounds can be lethal and in small amounts are very irritating to mucous membranes, producing an asthmatic type of effect. Great care must be taken in their use. Close medical supervision of workmen is desirable.

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A Study

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Received for publ
From the Institute
Department of Dern
gan Medical School.
This work was su
Grant RG5727(R1),
U.S. Public Health