DERMATITIS FROM SYNTHETIC RESINS

LOUIS SCHWARTZ, Medical Director

From the U. S. Public Health Service

Dermatitis is of frequent occurrence among workers making and using synthetic resins.

The number of synthetic resins manufactured and used is constantly increasing.

A resin, according to Ellis, (1) is a solid or semi-solid, complex, amorphous mixture of organic substances having no definite melting point and showing no tendency to crystallize. It is characterized by such physical properties as a typical lustre and a conchoidal fracture rather than by any definite chemical composition. The synthetic resins are often called plastics.

Resins are formed by (1) polymerization where a number of molecules of the same composition called monomers unite to form a larger molecule of the same composition called a polymer and by (2) condensation where a number of molecules not necessarily of similar composition unite to form a molecule dissimilar in composition to the components, some compounds being liberated.

In homopolymerization the polymer is built by additive combination of the monomer. In copolymerization two or more molecules polymerize at the same time to form a product the properties of which differ from that of each polymer alone. Heteropolymerization is a process where additive copolymerizable substances combine with a nonpolymerizable substance.

Chemicals known as catalysts are often used to affect polymerization and even to cause condensations. Catalysts are by definition supposed to act by their presence and not be affected by the chemical reaction which they induce.

Dermatitis is seldom caused by the completely polymerized, finished pure resin, or by the completely condensed, "cured" finished pure resin. The monomers and low polymers, and the incompletely condensed ("cured") resin, or the uncombined components, are the usual causes of dermatitis. The catalysts and the by-products may also be skin irritants. Many of the monomers are primary irritants as well as sensitizers. The same holds true for many of the components of resins made by condensation.

The skin irritating properties of the chemicals from which the resin is made are retained in the resin as long as these chemicals are uncombined, or so incompletely combined that the combination is still an irritant.

In resins formed by condensation of irritant compounds, the so-called first and second stages of "cure" are still skin irritants. The resin varnishes, glues, and molding powders usually fall into these two stages of cure. The "cure" is completed by the application of heat after the varnishes and glues are applied and as the powder is being molded.

The irritating properties of the monomers which combine to form polymers are retained in the polymerized resins as long as there is any monomer remaining.

1 From Dermatoses Section, Division of Industrial Hygiene, Bureau of State Services. Received for publication April 3, 1945.
in the resin or as long as there are low polymers in the resin which are skin irritants. The bi-mers are usually less irritating than the monomers, the tri-mers less than the bi-mers, etc.

Dermatitis is seldom caused by the completed condensation product, or by the completely polymerized resin. Exceptional cases may be those in which the completed resin is soluble in the secretions of the skin, and if the "cure" or polymerization is faulty or imperfect as in the case of "flash" in molded resins, or insufficiently cured resin varnishes and glues.

Many of the chemical components of resins are both primary irritants and sensitizers. Examples of such are phenols, aldehydes, allyl alcohol, styrene, acrylonitrile, vinyl monomers, and many others.

The synthetic resins may be divided into two types according to their reaction to heat (1) thermo-setting, (2) thermo-plastic. They may also be divided into two types according to their method of formation (1) resins formed by condensation, (2) resins formed by polymerization.

For the purposes of this paper, synthetic resins may be classified as follows:

1. Phenol-formaldehyde Condensation Thermo-setting
   a. Furfural-phenol-formaldehyde* Condensation Thermo-setting
   b. Lignin-aldehyde Condensation Thermo-setting
   c. Cashew nut shell liquid formaldehyde Condensation Thermo-setting
2. Urea-aldehyde Condensation Thermo-setting
3. A series of resins is formed by the condensation of aldehydes, particularly formaldehyde, with a group of chemicals of which urea is the simplest. Other chemicals in this series are dicyandiamide, melamine, and the sulfonamides, all of which will combine with aldehydes to form condensation resins. Most of these are of the thermo-setting type. Many of these are used in mixtures with each other to give resins with special properties. For example, we may encounter resins in which a mixture of melamine and urea is condensed with formaldehyde.
4. Ester gums Condensation Thermo-plastic
   These are made by condensation of the acids of natural resins with glycerol or glycols.
5. Alkyd resins
   These are condensation products of glycerols or glycols with polybasic acids, or anhydrides such as phthalic or maleic. Some are thermo-setting and some thermo-plastic. Many of these resins are used as coating and their cure is completed by air drying.
5a. Modified alkyds.
   These are combinations of alkyd resins with such chemicals as styrene, vinyl chloride, allyl alcohol, or other resins such as urea-formaldehyde. They may be made by polymerization or by condensation and are usually of the thermo-setting type.
6. Polyvinyl resins Polymerized thermo-plastic
   These are polymers or copolymers of vinyl chloride or acetate or acetal: vinylidine chloride and vinyl carbazole may be placed in this class.
7. Acrylate and methacrylates Polymerized thermo-plastics
8. Polystyrene Polymerized thermo-plastic
9. Allyl alcohol and allyl mod. alkyds Polymerized thermo-setting
10. Cumarone and Indene made from tar residue Polymerized thermo-plastic

*a. Furfural is an aldehyde.
   b. Lignin is a natural resin obtained from wood. It is a complex phenol reacting with aldehydes.
   c. Cashew nut shell liquid consists principally of complex phenols which can react with formaldehyde.
11. Cellulose nitrate and acetate: ethyl and methyl cellulose. These are derivatives of natural cellulose and are thermo-plastic.

12. Mixed types where two or more of the above types are combined.


14. Chlorinated resins. Thermo-plastic. These are made by chlorinating oils, balsams and waxes.


In addition to the above classes some nonresinous chemical products are modified by chlorination, oxidation, sulfurization, or heat, to form compounds which may be regarded as synthetic resins. Examples of such compounds are the solid chloronaphthalenes, chlorodiphenyls and chlorodiphenyl oxides.

The solid resins are used for making plastic panels, knobs, buttons, ornaments, bottle caps, dishes, glasses, dentures, wearing apparel, gears, rubber compounds, adhesive plaster, etc.

The semi-solid resins are used for glues, sizing: adhesives, wall boards, etc.

Solutions of the resins are used for lacquers, varnishes, floor finishes, fabric finishes, hair lacquers.

The phenol-aldehyde resins. These may be combinations of any of the phenolic compounds and any of the aldehydes.

They come in four principal forms:

1. The cast resin which is finished in the factory and from which solid objects are machined.

2. The molding resin, usually a powder, which is sold for molding objects, the cure being completed in the molding operation.

3. The semi-solid incompletely combined resin used for glues and sizings.

4. The resins or their solutions in various stages of cure for use as varnishes, lacquers, floor paints, etc.

The cast resin is made as follows:

Formaldehyde and ammonia are mixed in proper proportions in a kettle with either phenol, cresol, dimethyl ortho-cresol, or para-tertiary-amyl phenol, and heated a sufficient length of time and to the proper temperature. After combination takes place the compound is drawn out of the kettle in the form of a syrup, run into pans, and allowed to cool and solidify. This is known as first-stage resin or alpha resin. The pans are then heated, the resin remelted, and poured into suitable molds. The molds are placed in large carriers filled with mineral oil and placed in "curing" ovens where they are heated and go through the so-called beta and gamma stages into the completed cast resin. After being taken out of the oven the molds are removed from the oil, the resin is removed from the molds, and the oil washed off with soap and water, and dried. It is then ready to be carved, lathed, or bored into whatever object is desired.

During the course of these operations, formaldehyde is given off and the air of the room is strong with the odor of it unless adequate forced ventilation is employed. Workers in the rooms who are sensitive to formaldehyde may develop dermatitis of the face, neck, and arms, as well as of the covered parts where there is friction, such as the belt line, the angle at the shoe tops, and the wrists at the cuff line. Irritation of the conjunctiva and respiratory tract is common.

The oil used in the "curing" process dissolves out of the resin some of the phenols and formaldehyde and, if the oil is used over and over again without
purification, it contains considerable quantities of these substances; as much as two per cent each of phenol and formaldehyde in one sample analyzed. The men who handle this oil have their clothes splashed with it and at times suffer not only from oil acne and folliculitis of the legs, thighs, and other parts of the body touched by the oil-soaked clothing, but also from dermatitis due to the irritating action of the phenol and the formaldehyde. The eruption in these cases usually consists of diffuse erythema with scattered papules and pustules of an oil folliculitis.

The girls who wash the oil off the resin with soap and water may also develop dermatitis of the hands and arms from the irritants in the oil and also from the strong soap solution with which their hands are constantly wet. In many factories the oil is treated with sodium hydroxide after each baking in order to neutralize the phenol and formaldehyde. If this is not carefully done, dermatitis may result from too much alkali in the oil.

The skin hazards to the users of these cast resins are practically nil, since no phenol or formaldehyde is given off by the finished product.

Mayers (2) of the Division of Industrial Hygiene, New York State Department of Labor, performed patch tests on 61 people with these finished resins and obtained no reactions.

The molding resin is made up in numerous qualities, containing different proportions of phenol, formaldehyde, and ammonia. It is carried to the alpha or beta stage and then is ground, heated, and blended with wood dust, zinc stearate, soap, dyes, and hexamethylenetetramine in a mix mill. From this mill it is discharged to conveyors where it is air-cooled. While cooling, it forms lumps which are ground in mills to a powder suitable for molding. The workers who mix, grind, and pack the molding resin, are all exposed to the dust of the irritating chemicals it contains, as well as to the formaldehyde which it gives off, the odor of which permeates the rooms. Dermatitis is a frequent occurrence among workers in those occupations especially if the rooms are not properly ventilated and if the machines about which dust and fumes collect are not properly ventilated by suction ventilating hoods.

In one factory, where no great care was taken to allay and prevent dust, 10 per cent of the workers were affected with dermatitis during a period of one year. Patch tests performed on 10 cases with various types of resins showed that sensitivity to hexamethylenetetramine ("hexa") and to formaldehyde was the cause of 80 per cent of the occupational dermatitis in this plant. Sensitivity to phenol was also found, but in lesser degree than to formaldehyde and hexa. This is in accordance with Mayer's and Dolgoff's findings.

The actual cause of sensitization dermatitis from exposure to hexa and formaldehyde is the same—namely formaldehyde. This finally decomposes in the presence of heat and moisture into formic acid, which is a primary skin irritant.

The incidence of dermatitis in the manufacture of molding resins is directly related to the amount of dust in the air and the amount of formaldehyde and hexamethylenetetramine that the dust contains. Dermatitis usually occurs at the points of friction with the clothing, such as the wrists, belt line, the shoe
DERMATITIS FROM SYNTHETIC RESINS

tops, and collar line. It may, however, occur on the covered parts when clothing permeated with dust is worn for any length of time. The face, especially around the eyelids, is often affected. The eruption usually consists of scattered papules and vesicles on an erythematous base and is seldom disabling in character. Many workers have these eruptions for a large part of the year but continue to work. Sometimes the dermatitis disappears over the week end and returns on resuming work. New workers who are sensitive, are usually affected a few days after beginning work. If the case is a mild one and the worker continues to work, he often develops an immunity. If the dermatitis is so severe that the worker cannot continue working, but must stay away from work in order to get well, immunity does not always develop. Such workers should be removed to some other occupation, if they get recurrent attacks. There are also those who work for a considerable length of time without any trouble and suddenly develop a dermatitis. Such workers usually do not develop immunity but continue to have dermatitis of varying severity intermittently throughout the year as long as they work at that particular occupation.

Furfural resins. Furfural or furfuraldehyde (CH₅OC—COH) is obtained by treating oat hulls and corn-cobs with sulphuric acid, under steam and pressure. It is a colorless inflammable liquid which can be polymerized to form resins. It can also be combined with phenols, amines, ketones and casein to form resinous products. Most of the furfural resins are dark in color, but ivory colored resins can be made with casein mixtures.

The skin hazards connected with the manufacture and use of these resins are similar to those from the other aldehyde resins.

Cashew nut shell liquid-formaldehyde resin. Cashew nut shell liquid (C.N.S.L.) is obtained from the fruit of a tree belonging to the Anacardiacea. It consists principally of cardol and anacardol, both of which are higher phenols and closely related to the irritant principal of poison ivy and the irritant principals of other members of the same family.

There a number of different resins made from cashew nut shell liquid, but most of the dermatitis reported from these resins is among workers coming in contact with the insulating varnish (Harvel) made from it. In the experience of the author, there is no greater incidence of dermatitis from this varnish than there is from other varnishes made from other phenols and formaldehyde. The cashew nut shell liquid like phenol is a primary skin irritant and a sensitizer. Patch tests with it on 15 workers elicited reactions on all of them. The reactions varied from 2+ to 4+, being most severe on new workers, and less severe on most workers who have worked for longer periods in the plant, and least severe on most of those who actually handled the oil for many years. This shows that "hardening" frequently occurs to the sensitizing effect of the oil but of course it does not occur to its primary irritant effect. A few workers never develop a tolerance.

Patch tests with cashew nut shell liquid-formaldehyde resin in various stages of "cure" showed that its skin irritating properties decreased as the "cure" became more complete, until there were no reactions to the completely cured resin.

Patch tests with the active ingredients of cashew nut shell liquid (cardol and
anacardol) showed that they are primary irritants and sensitizers. Cardanol, the distillate obtained from cashew nut shell liquid which has been treated with sulphuric acid and partially polymerized, is a primary irritant but not as irritant as anacardol or cardol. Comparative patch tests with equivalent dilutions of anacardol and hydro-urushiol (an active irritant ingredient of poison ivy) showed that the poison ivy is a more powerful vesicant than anacardol.

Patch tests performed over skin covered with a poison ivy protective ointment (L.S.) showed that the ointment completely protected the skin from the action of anacardol, hydro-urushiol and acetone extract of poison ivy (Lederle).

Hexamethylenetetramine, formaldehyde, and paraformaldehyde are used in making C.N.S.L.-formaldehyde resins and much of the dermatitis among workers making the resins and among those using the incompletely cured varnish is due to the formaldehyde radical.

The prevention of dermatitis from C.N.S.L.-formaldehyde resins among the workers making and using them consists of the same measures as described under phenol-formaldehyde resins, namely, daily change of work clothes, wearing clean rubber or washable leather gloves, and impervious sleeves and aprons when working with the "uncured" resins; installation of wash stands at strategic places in the plant, and instructions to the workers to wash the hands and arms with soap and water immediately after they come in contact with the C.N.S.L., hexamethylenetetramine, paraformaldehyde, and partially cured resin. Rapid desensitization with injections of increasing concentrations of C.N.S.L. may be tried on those workers who cannot develop "hardening," as shown by repeated attacks of dermatitis over a long period of employment.

The treatment of acute cases of dermatitis from C.N.S.L. consists in the application of mild wet dressings in the vesicular stage (Burow’s solution 1:20; aqueous solution tannic acid 10 per cent) followed by mild ointments as the eruption dries and becomes scaly.

The Urea-aldehyde resins. Urea-aldehyde resins may be made of combinations of any form of urea and any aldehyde.

The most frequently used types are made by mixing urea and formaldehyde. No heat is required, the reaction generating its own heat. A syrupy liquid results. This is mixed with bleached sulphite pulp under heat and pressure and then dried in tray dryers. It is then mixed in a ball mill with pigments, zinc stearate, and a small amount of hexamethylenetetramine (about 0.5 per cent). It is finally screened and is ready for shipment. Minute amounts (fractions of one per cent) of other ingredients are added to different brands of urea-formaldehyde resins.

Dermatitis is less frequent among workers making urea-formaldehyde resins than among those making the phenol-formaldehyde type.

Among a group of 190 employees, there had occurred only four cases of dermatitis over a period of more than two years. They were all due to sensitivity to formaldehyde. Two chemists in the experimental laboratory of these plants were hypersensitive to formaldehyde and developed dermatitis when exposed to it. One of them could expose his forearm to the mouth of an open bottle of
formalin and almost immediately an erythema would appear on the exposed skin. Horsfall records the case of a man who after long exposure to formaldehyde became so sensitive that he reacted to a dilution of 1 part in 8,000,000.

The process of molding powders is practically the same for all the resins. The powder is placed in a “pill machine” and pressed into proper sizes for the molds. The “-pills” are issued to the molders who put them into the molds where they are subjected to heat and pressure which shapes and hardens them. During the molding process, gases are given off from the molds and the odor of formaldehyde in the room is strong, irritating the nose, throat, and eyes of those unaccustomed to it. The concentration of formaldehyde is especially strong over the molding machines and the molders often suffer from dermatitis due to these fumes. This dermatitis may affect the face, neck, and arms.

There is an excess of powder in the molds which flows out during the molding process and is only partially “cured.” This is called the “flash.” When the molds are opened, the “flash” is cleaned off the molds by the molders and those sensitive to the formaldehyde or phenol in the imperfectly “cured” dust, develop dermatitis on the hands or forearms. Girls are usually employed to file “flash” off molded objects (finishing and inspecting) and dermatitis is quite frequent among them. The forearms are usually affected by the dust of the imperfectly cured “flash” especially from the phenol-formaldehyde resins, although it may occur from the urea-formaldehyde resins.

The worker who handles the molding powder in order to place it in the “pill” machine and issues it to the molders is also exposed to a skin hazard from the materials which he handles. The dermatitis of the molder, however, usually occurs on the wrists and the palms. The dermatitis of the palms manifests itself in the form of a chronic fissured eczema, whereas that on the wrists is of the erythematous vesicular type.

That hexamethylenetetramine is a large causative factor in dermatitis caused by these resins is indicated by the fact that most of the cases have occurred among workers handling the phenol-formaldehyde resins which contain many times more of the hexamethylenetetramine than do the urea-formaldehyde resins. Hexa, formerly used in the rubber industry as an accelerator, has caused many cases of dermatitis but has now been almost entirely displaced by other accelerators. It is a necessary ingredient of certain phenol-formaldehyde molding powders because it furnishes the necessary amount of formaldehyde and ammonia for the resin to go through the gamma stage, or to completion in the molding process. In the urea-formaldehyde resin, hexa acts as a stabilizer to prevent the resin from hardening before it is molded. Less than 1 per cent of it is used in the resin.

Dermatitis among the users of molded phenol-formaldehyde and urea-formaldehyde resins is rare, but may occur if any of the “flash” is left on the object or if the molding process is not completed and the hexa is not all combined. Theoretically all the hexamethylenetetramine is combined in the completed resin, but practically, in some imperfectly cured pieces or in pieces where too much
hexa has been used in the molding compound, there may be a sufficient amount left in the finished object to cause dermatitis among hypersensitive users. The same thing may be true of the phenol content.

Blumenthal and Jaffe (3) described seven cases who had weeping eczema on the uncovered portions of the body, especially the hands. All of these patients worked with "bakelite" varnish. Patch tests showed that the "bakelite" in the varnish was the cause of the eczema and that all who developed eczema were hypersensitive to phenol. The composition of the "bakelite" varnish was not given.

Melamine resins. The melamine resins are made by polymerizing dicyanidiamine to form melamine, a white powder which can be combined with formaldehyde or with urea-formaldehyde to form a resin. Dermatitis may occur in its manufacture chiefly due to formaldehyde as described under urea-formaldehyde resins.

The melamine resins can be used for the same purpose as the urea-formaldehyde resins. Dermatitis from melamine resin glues has been reported in the manufacture of plywood and laminated products.

In a plant where fabrics were laminated with a melamine resin and then molded into airplane engine exhausts and then heat cured, dermatitis occurred among the workers who handled the uncured moist laminated fabrics as they came out of the liquid resin dip; as they were being cut to shape; as they were molded onto forms, and as they were trimmed and finished after being cured.

Patch tests with the liquid resin and with the uncured laminated fabric gave severe reactions on those affected. Patch tests with the cured laminated fabric gave milder reactions. This showed that the "cure" was not complete. This particular melamine resin contained 10 per cent by weight of resorcinol.

Sulphonamide formaldehyde resins. The sulphonamide-aldehyde resins are made by combining p-sulphonamide, (a by-product in the manufacture of saccharin from toluene) with formaldehyde. They are soluble in alcohol and acetone and are used in varnishes and lacquers.

Because they are mixable with solutions of cellulose nitrate and acetate, the sulphonamide-formaldehyde resins have been used as adhesives and plasticizers in nail lacquers. Many cases of dermatitis from nail lacquer have been traced to the sulphonamide-formaldehyde resin contained therein.

Ester gums. Ester gums are usually glyceryl, methyl, and ethyl esters of abietic acid. They may be combinations of any of the natural resins with glycerol, ethylene glycols, other polyhydric alcohols, phenols, naphthols, and drying oils.

Ester gums are used in paints, enamels, lacquers, varnishes, fabric finishes, adhesive plaster, paper sizing, and even as emulsifying and wetting agents. (Rosin soaps.)

The ester gums are made in closed kettles and no cases of dermatitis were observed among the workers, but an outbreak of dermatitis occurred among people

\(^2\) "Bakelite" is the trade name of a variety of synthetic resins.
wearing fabrics finished with a preparation of an ester-gum, and the ester-gum was proven to be the actual irritant (4).

**Alkyd resins.** Alkyd resins are combinations of polybasic acids and polyhydric alcohols. They are usually combinations of phthalic anhydride or maleic anhydride with glycerol, ethylene, or propylene glycols, mannitol or sorbitol. The polybasic acids may also be combined with drying oils and natural resins. They are used to protect metal surfaces, such as automobile lacquers, for printing inks, laminating glass or wood, or paper, abrasive wheel bindings, etc.

The manufacturing process consists of cooking the chemicals in closed kettles. An occasional case of dermatitis occurs from phthalic or maleic anhydride, and from solvents used to place the finished resins into lacquer or varnish form. Phthalic acid is a sensitizer and maleic acid is a primary irritant and sensitizer.

Dermatitis occurs in the use of these resins as adhesives for laminating wood and fabrics.

An outbreak of dermatitis from hair lacquer was traced to the use of a resin formed from maleic anhydride and rosin, which was used as a substitute for shellac, the usual ingredient (5).

**Modified alkyd resin.** The alkyd resins are frequently modified by combination with other resin forming chemicals. Combinations with melamine-formaldehyde resins have been reported to cause dermatitis among workers handling the partially cured resin. Combinations of alkyd resins with glycols and styrene or vinyl chloride, or allyl alcohol, are extensively used for laminating purposes. These combinations form liquid or soft paste-like monomers which are primary skin irritants and have caused extensive outbreaks of dermatitis among workers handling them. The further polymerization proceeds, the less the irritant powers of the resin until the completely cured resin is innocuous. Imperfectly cured pieces, however, or ‘‘flash’’ may cause dermatitis.

In a factory where Radar casings were being made from a modified alkyd resin and fiberglas, a large number of cases of dermatitis occurred. The resin is made by condensing styrene with maleic acid and diethylene glycol to form the monomer. The monomer is a straw colored paste-like substance with a pungent, irritating, suffocating odor, which will soon cause irritation of the eyes and nose and throat. If permitted to stay on the skin for a few minutes it will cause stinging and erythema, and if it stays on for an hour or two it will cause blisters. This substance is not only a primary irritant, but also a sensitizer: so that many who develop a primary irritation also become sensitized and develop dermatitis from exposures which are so slight, that they would have had but little effect before sensitization.

The manufacturing process in this factory was as follows:

A roll of fiberglas is degummed and then passed through the resin to which benzoyl peroxide has been added (1½ per cent). The sheet of fiberglas is then passed through a roll to force the resin into it. The sheet is cut into suitable lengths and placed on a form. A sufficient number of sheets are smoothed down on the mold by pressure of the hands. The top of the mold is then put on (a piece of cellophane is interposed between the sheets and the top of the mold) and the mold is placed in the curing cylinder where the heat is applied. When the cured mold is taken out of the cylinder, the resin sheet is trimmed to size, the ‘‘flash’’ being removed. All these operations entail handling the resin.
Dermatitis even occurs among those handling the fiberglass. This is due to mechanical irritation of the glass fiber and the rubbing into the skin of the resin binder on the glass fiber. Workers handling the glass fiber should wear gloves and sleeves.

The following preventive recommendations were made:

1. Those girls who handle the resin-impregnated sheets should also wear gloves (the fingers may be cut so as to enable easier manipulation). Long sleeved smocks should also be worn. The gloves (preferably washable leather) and the smocks should be cleaned at least once a day. Those whose jobs require handling the resin paste should wear long rubber gauntlets.

2. Those employed at places or occupations where there is a strong concentration of fumes should be provided with a protective ointment for the face and neck, of the type which leaves a dry adherent water-repellent coat on the skin to shield it from fumes. This ointment may also be applied to uncovered parts of the fingers.

3. Well placed ventilators to draw fumes away from the workers.

4. The use of broad spatulas with handles to smooth the resin impregnated fiberglass down over the molds. This would eliminate much of the contact with the resin.

5. Placing wash stands close to the workers and instructing them to wash the resin from the hands and fingers at frequent intervals.

6. Instructing workers not to touch face and neck with resin-soiled hands.

Polyvinyl resins. These are thermo-plastic resins made by polymerization of vinyl acetate, or vinyl chloride, or copolymerization of the two. Polyvinyl alcohol resins and combinations such as butaryl acetal of polyvinyl alcohol, and vinyl carbazole may also be included in this class.

Vinyl resins are used for wearing apparel, lamination of fabrics, electric insulators, lining of tin cans, dentures, molding purposes, phonograph records, and many other purposes. No cases of dermatitis have been reported in the manufacture of vinyl acetate or vinyl chloride and their polymers, but dermatitis has occurred from wearing wrist-watch straps, garters, and suspenders made of the polyvinyl copolymers (6). The actual irritants in the wearing apparel were found to be the plasticizers and stabilizers contained in the resin (dibutyl tin maleate and dibutyl sebacate). Workers engaged in coating fabrics with the copolymer of vinyl chloride and vinyl acetate were affected with dermatitis which was found to be due to a by-product formed in the recovered acetone solvent during the recovery process. The chemical formed was bi-acetyl. When the biacetyl was removed the outbreak of dermatitis ceased.

Vinyl carbazole is used as an electrical insulator and the monomer, a white powder, is a strong sensitizer. It causes considerable dermatitis among those in contact with it. The polymer formed by heating the monomer is also a sensitizer but not as strong as the monomer (7).

Butaryl acetal of polyvinyl alcohol is made from polyvinyl acetate, which is hydrolized to polyvinyl alcohol and this is condensed with butaryl aldehyde.
The resin is plasticized and made into a water-white sheet used in making shatterproof glass. The sheets of the resin are powdered with sodium bicarbonate so as to prevent them from adhering to each other in shipment. Dermatitis has occurred among workers applying the sodium bicarbonate and among workers in the safety glass factory who separate the sheets. The dermatitis is caused by the sodium bicarbonate being converted to sodium carbonate, which is the actual irritant. Workers exposed to the sodium carbonate sometimes have their hair bleached to a blond color. Workers handling sheets of resin treated with sodium bicarbonate should wear impervious gloves, sleeves, aprons, and caps. They should be furnished with clean work clothes daily and take showers before going home from work.

The vinyl radical can be combined with a glycerol and dibasic acid resin to form modified alkyd monomers which polymerize (with the catalytic aid of an organic peroxide and heat) into thermo-hardened resins (see alkyd resins).

**Acrylic and methacrylic acid resins.** These acids are colorless liquids which polymerize and the polymerized ethyl and methyl esters form resins which can be used as glues for adhesion to glass. They can be polymerized to form transparent sheets used for windows, lenses, and transparent plastics. The monomer can be used as the plasticizer.

Methyl methacrylate is polymerized by the action of heat in the presence of benzoyl peroxide to form a clear transparent resin used for many purposes (Lucite and Plexiglass). Dermatitis has occurred among dental technicians molding it to make dentures. The actual irritant is said to be the monomer, a water-white liquid, used to plasticize the resin mass. The catalyst, benzoyl peroxide may also cause dermatitis.

The prevention of dermatitis among dental technicians from the resins used for making dentures consists in wearing rubber gloves and impervious sleeves and aprons.

**Polystyrene resins.** Styrene (C6H5—C(=CH)2) is a colorless liquid, b.p. 143°C. It is a fat solvent and primary skin irritant. It can be polymerized into a hard colorless thermo-plastic resin by dissolving it in ethyl benzene and heating in the presence of a catalyst (benzoyl peroxide).

The polystyrene resins are used for lacquers, molding, insulators, laminating glass, etc.

The copolymers of styrene and butadiene form the synthetic rubber Buna S, and the copolymer with acrylonitrile forms the synthetic rubber Buna N. Dermatitis occurs in the manufacture of styrene and in the manufacture of synthetic rubber from styrene (8).

Styrene is also used to modify the alkyd resins. The monomer made by condensation with glycerols and a dibasic acid is polymerized into a thermo-hardened polymer, by means of a catalyst (organic peroxide). The monomer is a primary skin irritant. (See modified alkyd resins.)

** Allyl resins.** These are among the newest of resins. They are made from allyl alcohol, a water-white liquid of low boiling point. It is soluble in water, alcohol and ether. It
volatilizes readily and gives off pungent vapors which irritate the mucous membranes and the skin.

Allyl alcohol is combined with a dibasic acid like phthalic, maleic, carbonic, oxalic, etc. to form liquid monomers. These monomers are more or less thick, viscid, clear liquids which are primary skin irritants and sensitizers.

The monomers can be polymerized into solids by adding benzoyl peroxide and heating. The completely polymerized resins are thermo-setting. No pressure and but little heat is required to polymerize the monomers and form laminated materials by the use of these resins.

Considerable dermatitis has occurred among workers making and using allyl resins. Although the monomers are primary irritants, older workers often continue work without much trouble both because of carefulness in not permitting the resin to stay on their skin for any length of time, and because they become "hardened" to the sensitizing effect of the resins. The completely polymerized resins are inert.

The allyl resins are used for laminating fiberglass to make gasoline tank linings; to make suitcases, etc.

**Cumarone resins.** Cumarone resin is made from the crude coal tar distillate which comes off between 150\(^\circ\) and 200\(^\circ\)C. This is redistilled to remove impurities and a sharply fractionated naphtha is obtained. This is treated with sulphuric acid to remove readily polymerizable hydrocarbons and to dry the naphtha. The tar and sludge are allowed to settle out and the remaining oil is pumped into a tank and treated with caustic soda. The oil is then distilled, the naphtha and naphthalene removed, leaving a heavy oil which boils between 320° and 330°C., and cumarone resin.

The process is almost totally enclosed and there are no special skin hazards with the exception of acid and alkali burns.

There are various grades of cumarone resin, the darker ones being used in varnishes, adhesives, rubber, paint, printing inks, and waterproofing, while the purest and whitest are sometimes used in chewing gum. The darker grades of cumarone resin may contain sulphonic acids and tar acids if they are not carefully prepared and it is probably these acids which cause dermatitis. The melanosis and photosensitivity described under coal tar is sometimes seen among workers who make cumarone resin where the process is not totally enclosed.

Dermatitis occurred from the darker cumaron resins in a varnish which was used on heddle frames in a cotton mill. The forearms of the weavers were struck continuously by the moving heddle frames coated with this varnish and some of the workers developed dermatitis on the forearms at the points of contact with the heddle frames. Patch tests showed that they were sensitive to chlorinated ceresin and cumarone resin in the varnish.

**Cellulose resins.** Celluloid or Pyroxylin are trade names for a material made of scraps of cellulose nitrate or cellulose acetate which are mixed with camphor and various plasticizers such as tricresyl phosphate, dibutyl phthalate, dimethyl phthalate, and solvents such as alcohol, acetone, ethyl acetate, amyl acetate, etc.

Dermatitis is rare but has been reported among workers who manufacture these products.
Laminating fabrics with resins. The fabric is usually passed through a solution or liquid phase of the A stage resin which is forced into the fabric. It is then partially cured by heating and then cut into the desired shapes and sizes. The pieces are then placed one on top of the other until the desired thickness is attained. The thick layers are then formed into the desired shape by fitting over forms and trimming. These are then placed into molds and the cure completed by heat and pressure. Any "flash" or irregularities are then trimmed off.

Dermatitis occurs frequently among those handling or in contact with the partially cured resin-impregnated fabrics. It usually affects the hands, forearms, neck, and face. It may be merely an erythema, or erythema with papules, vesicles and crusts.

Protective measures consist in the wearing of impervious sleeves, aprons, and fingerless gloves, as well as a protective ointment, either of the lanolin-castor oil type, or of the dry type.

Dermatitis also occurs among those handling the finished objects. Patch tests with the finished object were positive in those affected. This shows that the resin is not completely cured or polymerized and should receive a longer final "cure."

Some of the monomers of the thermo-setting polymerized resins are primary skin irritants. Especially is this true of a number of the modified alkyd resins used for laminating fabrics, glass fibers, and wood veneers. The modified alkyd resins containing styrene or allyl alcohol combined with an alkyd resin such as combinations of glycols and phthalic or maleic anhydride have been found to be particularly irritating in the partially polymerized stage. In one factory using these types of resins for laminated glass fabrics there was a labor turnover of 600 per cent among 85 workers in one year. There is no hardening to the primary irritant action of these monomers.

Modified alkyd resins of this type are sometimes miscalled styrene resins or allyl resins depending on the modifying molecule.

Resin glues. An increased use of glues is entailed in the manufacture of modern laminated products. With this there has been an increase in occupational dermatitis.

The resin glues are usually incompletely polymerized or incompletely cured resins, or solutions of resins, all of which are either primary skin irritants or sensitizers. In one plywood factory employing about 800 workers, 600 cases of dermatitis occurred in the first six months of operation. In another factory making tool handles from laminated glass and employing 100 workers, there was a labor turnover of 40 per month during the first six months of operation.

The resin glues are used in the manufacture of plywood, fiberboard, laminated asbestos, glass fabric, tool handles, coatings for fabric and paper, making rocket tubes, and many other purposes.

Composition of glues. Glue compositions vary widely. They can be roughly classified as (1) protein glues, (2) natural resin glues, (3) synthetic resin glues, (4) combinations of the foregoing.

Catalysts may be used in glues containing the synthetic resins.
The protein glues can be made from gelatin, hides, bone, cartilage, casein, isinglass (air bladder of the fish), fish heads (cod, haddock, hake), and vegetable protein (soya bean).

The natural resin glues may be made from dextrin, gum arabic, acacia, shellac, copal, dammar, rosin, etc. To any of these may be added such chemicals as sodium silicate, sodium hydroxide, sodium fluoride, zinc chloride, and copper salts. It is evident that a glue, the name of which may lead one to think that it is quite harmless (gelatin glue, casein glue), may actually contain powerful primary skin irritants.

The following synthetic resins, either alone or in combination with each other or with natural resins, may be used as liquid cold glues, thermal-setting glues, or molding powder glues: cumarone, polyvinyl esters, ethyl esters, methyl esters, cellulose esters, cellulose nitrate, alkyd, urea-formaldehyde, phenol-formaldehyde, melamine-formaldehyde, melamine-urea, allyl and styrene.

In the manufacture of these synthetic glues, catalysts are often added. For this purpose mineral acids (HCl or H₂SO₄), alkalies (NaOH, KOH, CaO, NH₄OH, etc.), zinc oxide, potassium cyanide, hydrazines, amines, hydrochloride, sodium ethyl sulfate, and organic peroxides. The completely polymerized or cured resins rarely cause dermatitis, but completely polymerized resins can seldom be used as glues. The incompletely polymerized or partially cured resins are the ones most used as adhesives and these contain the incompletely combined irritant chemicals which can and do cause dermatitis. The addition of the catalysts, many of which are themselves primary irritants, increases the skin irritant properties of resin glues.

The urea-formaldehyde, the phenol-formaldehyde, allyl modified alkyds, and melamine-formaldehyde resin adhesives are the ones most frequently reported as causes of dermatitis.

To determine the irritating chemical radical causing the dermatitis, the actual composition of the resin and the stage of polymerization should be known before patch tests can be performed intelligently. This information must be obtained from the manufacturers, as chemical analysis often fails in this respect.

In studies of dermatitis from resin molding powders it was found that formaldehyde was the chief irritant in phenol-formaldehyde resins, being responsible for about four-fifths of the cases. Hexamethylenetetramine, which is present in many of the molding powders to supply the additional formaldehyde needed to complete the cure in the mold, is not present in the glues. But, since formaldehyde is present in the urea and phenol-formaldehyde glues, the absence of hexamethylenetetramine does not deprive them of their skin irritative properties. The presence of phenols and formaldehyde in the glues can often be detected by the odor.

They are used in powder form, paste form, in solution, and as cold glues, or thermal-setting glues (with the addition of pressure).

These glues are primary skin irritants if they come in contact with the skin in sufficient concentration. That these glues are also sensitizers is proved by the fact that the workers having dermatitis react more rapidly to patch tests than
do the controls, as well as by the fact that about 50 per cent of the affected workers, if they are permitted to work while undergoing treatment, develop a tolerance to limited contact with the glues containing comparatively weak concentrations of the irritant chemicals.

In making plywood for planes and gliders, those who apply the cold liquid glues to the edges of the sheets of wood and those who apply the glue tapes (Tego) to the surface of the panels to cover defects are the ones most likely to be affected with dermatitis. The parts most often affected are the palms where they contact glue-soiled brush handles and spatulas, the dorsum of the hands, from glue-soiled washing solutions and glue-soaked sponges, and the forearms which are touched with glue-soiled fingers and tools. Those who work without stockings while shaping the panels in the molds often develop dermatitis on the legs where the glue touches the skin.

In some cases dermatitis begins as early as the third day after exposure (the primary irritant effect of the glue) while others may be exposed several weeks before dermatitis occurs. No doubt the degree of exposure to the glues and the personal cleanliness of the worker are the main factors determining the time of onset of dermatitis.

Those working on the presses, which heat and press together the sheets causing them to adhere and form plywood, are only occasionally affected. These workers are subjected mainly to the fumes of formaldehyde coming off the presses and only occasionally to contact with the uncured glue.

In factories where plywood propellers and other rigid parts are made, the contact is somewhat different. Here the pieces of veneer are impregnated with liquid resin glue by dipping them into a vat and then placing them in a pressure chamber. The workers at this operation are exposed to strong fumes of formaldehyde and to splashes of liquid. Unless properly protected these men will develop dermatitis, conjunctivitis, and irritation of the respiratory tract. Those engaged in mixing the glues are similarly exposed. Workers who machine, sandpaper, and polish plywood, are exposed to wood and resin dusts. Some of the plywood is machined before the resin glue is completely cured and at such operations there is more dermatitis than at operations where the completely cured resin dust is encountered.

In factories where glass cloth is made into tool handles and translucent partitions, workers thought the glass fabric was the cause of the dermatitis, but patch tests showed that the condition was caused by phenol-formaldehyde molding powder which is spread on the fabric before it is placed in the hot pressure molds. The operation of placing the molding resin powder on the cloth should be performed in such a manner that the resin powder does not come in contact with the worker.

The catalysts used in these factories were ammonium chloride, ammonium sulfate, oxalic acid ester, hypophosphorous acid ester, and benzoyl peroxide, laurol peroxide, para tertiary butyl benzoate.

The principles of treatment of dermatitis caused by the glues are the same as for any other form of contact dermatitis. In the acute stages where there is
edema, vesicles, and oozing, only soothing wet dressings should be used, such as boric acid solution, Burow's solution, and tannic acid solution 3 to 5 per cent, this last on parts other than the face or neck. In the later stages, when the eruption begins to dry and crust, the use of mild fatty-base ointments such as boric acid ointment, calamine ointment, or zinc oxide ointment should be used. The use of phenols for antipruritic purposes should be avoided, because they may increase the dermatitis. If complications, such as infection, set in, special treatment may be required. Workers with mild cases should be given protective clothing, and should be treated on the job in order to give them the chance to become "hardened" (if the dermatitis is caused by allergy) and to learn how to protect themselves (if it is due to primary irritation).

To prevent dermatitis among workers with resin glues, the management should first of all provide suitable exhausts to draw away from the workers all irritant dusts or fumes coming off the operations. The management should provide, daily, clean coveralls for all workers exposed to irritant glues, dusts, and fumes.

Workers who apply the glues to the veneer should be provided with impervious gloves made either of washable leather or fabric-lined rubber, and sleeves and aprons of impervious materials (10). The sleeves should fasten over the gloves at the wrist to prevent irritants from falling into the gloves.

Facilities for washing the hands with soap and running water should be installed at strategic places so that the workers can frequently wash glue from the gloves and skin. The brushes and sponges used for glueing should be washed or changed about every two hours and workers should be cautioned against touching the face and other parts of the body with glue-soiled fingers, gloves, or tools.

Sufficient shower baths should be provided for workers, and they should be compelled to take showers after work. Sufficient time should be allowed for this and the workers should be paid for the time.

Protective ointments or applications are not necessary if these precautions are observed, but if they are used they should be furnished by the management and should be used in addition to all of the other preventive measures. The type of applications best suited to prevent glues from touching the skin are those of the water-insoluble invisible glove type, or of the water-repellent fatty type.

BIBLIOGRAPHY


(9) Schwartz, Louis, Peck, Samuel M., and Dunn, J. E.: Dermatitis from Resin Glues in War Industries, Public Health Reports, 58: 899-904 (June 11) 1943.