Dermatitis from Synthetic Resins and Waxes*

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DERMATITIS in the manufacture of natural resins and from their use has been reported by numerous observers,[1] but dermatitis in the manufacture of synthetic resins and from their use has not been frequently reported [2] or studied.

The principal synthetic resins manufactured in the United States are:

1. Phenol-formaldehyde resins, sold under various trade names, such as Bakelite, Durite, Durez, Resinox, Indur, etc.
2. Urea-formaldehyde resins, sold under trade names such as Beetle, Plaskon, Unite
3. Coumaron resin, made from coal tar residue
4. Ester gums, which are natural resins, such as Rosin, Dammar and Copal, in which the acid of the resin has been combined and neutralized with glycerol
5. The glyptal resins, which are a combination of glycerol and an organic acid, such as phthalic and malleic acids
6. The vinyl resins, which are vinyl esters, ethers or halides combined with phenol, formaldehyde and hexamethylenetetramine
7. Furfural resins, obtained from combining furfural with phenol (furfural obtained from corn cobs by treating with H_2SO_4 and fractional distillation)
8. Chlorinated resins, obtained by chlorinating various oils and balsams
9. Chlorinated waxes, obtained by chlorinating mineral oils, paraffin, naphthalene, di-phenyl, etc.

These resins are used for many purposes:

For making plastics, such as telephone receivers, pipe stems, push buttons, ear phones, cigar holders, bottle caps, buttons, inks, artificial teeth plates, ornaments, bracelets, earrings.

For making varnishes, flexible coatings, floor finishes.

For making cements, wall boards, gears, dishes, water containers, insulators, rubber compounds, and numerous other objects and for electrical insulations on condensers and wires.

The most important of the resins, from a standpoint of volume used and skin hazards, are the phenol-formaldehyde, the urea-formaldehyde and the coumaron resins.

PHENOL-FORMALDEHYDE RESINS

These are made in two principal varieties:

1. The cast resin, which is finished in the factory
2. The molding resin, which is sold to molding companies and completed in the molding process

Phenol or cresol, formaldehyde and ammonia are mixed in proper proportions in a kettle and heated a sufficient length of time and to the proper temperature.[3] They combine and are drawn out of the kettle in the form of a syrup. This is run into pans and allowed to cool, when it solidifies. This is known as "first stage resin," or "alpha resin." The pans are then heated, the resin re-melted and poured into suitable molds. These are placed in large, mineral oil filled carriers and

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placed into *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 resin is taken out of the molds and oil, and washed with soap and water and dried, and it is then ready to be carved or 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 ankle at the shoe top, and the wrist at the cuff line.

The oil used in the curing process dissolves out of the resin some of the phenol and formaldehyde and, if used over and over again, it can contain considerable quantities of these substances. One sample which was analyzed after it came out of the ovens contained 2 per cent each of phenol and formaldehyde. The men handling this oil have their clothes splashed with it and at times suffer not only from oil acne and dermatitis of the legs, thighs, and other parts touched by the oil-soaked clothing, but also from dermatitis due to the irritating action of the phenol and the formaldehyde contained in the oil. The eruption in these cases is usually a diffuse erythematous base on which there are scattered the papules and pustules of an oil folliculitis.

The girls washing the oil off the resin, with soap and water, may also develop dermatitis of the hands and arms from 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 hydrate after each baking in order to neutralize the phenol and formaldehyde it may contain, but if this is not carefully done, dermatitis may result from too much alkali.

The skin hazards to the users of these cast resins are practically nil, because when they are finished no phenol or formaldehyde are given off from them.

The molding resin is made up in numerous qualities, containing different proportions of phenol and formaldehyde and ammonia. It is carried to the alpha stage or beta stage, and then is ground, heated, and mixed with ground wood, zinc stearate, soap, dyes, and hexamethylenetetramine in a mix mill. From this mill it is discharged on to conveyors, where it is air cooled. While cooling, it forms lumps which are ground in mills to proper sizes fit for molding. The workers engaged in mixing, grinding, and packing 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 in this occupation, especially if the rooms are not properly ventilated to draw off dust, and if the machines and jobs where there is dust are not properly protected by suction hoods.

In a factory employing about 400 workers, where no great care was taken to allay and prevent dust, 27 cases of dermatitis occurred in 8 months. Patch tests performed on 10 cases with various resins, hexa, 4 per cent solution of formaldehyde, and 2 per cent solution of phenol, showed that hypersensitivity to hexamethylenetetramine and to formaldehyde was the cause of 80 per cent of the occupational dermatitis in this plant. Hypersensitivity to phenol was also found, but in lesser degree than to formaldehyde and hexa.

The actual cause of dermatitis from exposure to hexa and formaldehyde is the same. They both finally decompose in the presence of warmth and moisture

into formic acid, which is the real skin irritant.

Dermatitis from the dust of the molding resins usually occurs at the points of friction with the clothing—the wrist, the belt line, the shoe tops and the collar line. It may, however, occur on the covered parts when the dust penetrates the clothing. The skin around the eyelids may also be affected. The eruption consists, usually, of scattered papules and vesicles on an erythematous base.

It gets well if the worker stays away from work, and returns again if he resumes work. In this factory, the dermatitis was more prevalent in the winter because the workers did not take showers in cold weather after their shift, whereas in the summer they were more likely to do so.

UREA-FORMALDEHYDE RESINS

These are made by mixing urea and formaldehyde in a kettle. 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 dried in tray dryers. It is then mixed in a ball mill with pigments, zinc stearate, and a small amount of hexamethylenetetramine, about ½ per cent. It is then screened, and is ready for shipment. Minute amounts (fractions of 1 per cent) of other ingredients are added to different brands.

The manufacture of the urea-formaldehyde resins on a commercial scale is more recent than that of the phenol-formaldehyde resins, hence the two factories studied had more modern machinery and safety appliances than the phenol-formaldehyde resin factories. There were adequate ventilation facilities and good facilities for dust prevention. As a result, among 190 employees over a period of over 2 years, there had occurred only 4 cases of dermatitis. They were all due to hypersensitivity to formaldehyde. Two chemists in the experimental laboratory of these plants were hypersensitive to formaldehyde and suffered with dermatitis when exposed to it. One of them exposed his forearm in my presence to the mouth of an open bottle of formalin and almost immediately an erythema developed on the exposed skin.

In a molding plant in Ohio employing about 300 workers, where phenol-formaldehyde and urea-formaldehyde resins are used, 26 cases of dermatitis occurred in the first 10 months of 1934, and in a molding plant in Pennsylvania half of the workers developed dermatitis in the hot months of 1935.

The process of molding is practically the same for all the resins. The powder is placed in a "pill machine" and pressed into proper shapes for the molds. The pills are then placed 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 is strong in the room and irritates the nose and throat and eyes of those unaccustomed to it.

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 and filed off the molded object.

Patch tests with the resins with which they worked were performed in the winter on 2 active cases of dermatitis, and 10 workers who had recovered from dermatitis, gave only 2 positive reactions, 1 to the phenol-formaldehyde and 1 to the urea-formaldehyde resin. The examination and history of the 10 cases who had dermatitis but were free of it when the patch tests were made, showed that 2 had dermatophytosis and 1 probably had ptyriasis rosea. It

is probable that a considerable number of the 26 cases reported in 1934 were not of industrial origin.

The same plant was visited in August, 1935. Twelve cases of dermatitis had occurred since the first visit 9 months before. This time 9 workers who had dermatitis during this period were patched with suspected samples of urea-formaldehyde and phenol-formaldehyde resins, as well as with hexamethylenetetramine. Four showed no reactions after 24 hours to any of the 7 patches applied. Five showed positive reactions to one or more of the resins, and of these 5, 3 showed positive reactions to hexamethylenetetramine.

Two of the 4 cases who showed no reaction had eruptions at the time the patches were applied. One was a case of dermatophytosis and the other an eczema which dated back to childhood. The weather was cold (less than 70°) during the period the patches were on, and this may have a bearing on the reactions, because, of the 26 cases reported in 1934, 18 had occurred during periods of hot weather in May, June, July, and August.

There can be little doubt that a considerable percentage of the dermatitis in this plant was of occupational origin.

That hexamethylenetetramine is a major causative factor, is shown by the fact that most of the cases occurred in workers handling the phenol-formaldehyde resin, which contains more of it than does the urea-formaldehyde resin.

Hexa, which was extensively used in the rubber industry as an accelerator and caused dermatitis, has now been almost entirely displaced by other accelerators. It is necessary in certain phenol-formaldehyde molding resins in order to furnish the necessary amount of formaldehyde and ammonia required to go through the gamma stage—or to completion.

In the urea-formaldehyde resin, hexa acts as a stabilizer to prevent the resin from hardening before it is molded.

The ventilating and dust prevention conditions in the molding plants were poor. There were no suction hoods over the molding machines. The suction hood over the "pill machine" was out of order. There was only window ventilation in the workrooms, and wash-ups or showers after work were not compulsory. With proper dust allaying facilities, such as forced ventilation, suction hoods, wet sweeping of floors after each shift, compulsory showers, protective clothing and ointments, the incidence of dermatitis in this plant could be decreased.

Dermatitis may occur in users of molded phenol-formaldehyde and urea-formaldehyde resin wares if the hexa is not all combined. Theoretically, it is all combined in the completed resin, but practically (as in some imperfectly cured pieces or pieces in which there was too much hexa in the molding compound to be completely taken up), there may be a sufficient amount remaining to cause dermatitis in hypersensitive people. The same thing may be true of the phenol, if not completely combined.

Dermatitis has been reported as due to contact with finished resin products, such as dermatitis of the ear from telephone receivers, and of the hands from varnishes.

In order to show that a dermatitis may have been caused by contact with a resin, it must be established that:

1. The dermatitis followed contact with the resin
2. That portion of the skin which came in contact with the resin was first affected
3. A powdered portion of the suspected resin placed on the clear skin near the eruption in the form of a patch test, gives a positive reaction if left on 24–96 hours

To determine the actual chemical in the resin which caused the dermatitis,

the nature and chemical composition of the resin must be determined, and patch tests performed on the patient with each of the chemicals composing the resin in order to determine to which of them the patient is hypersensitive.

The patches of the chemicals should be in such dilutions as will not cause reaction on the normal skin if allowed to remain on for 24 hours.

A 2 per cent aqueous solution of phenol can remain on the normal skin in the form of a patch test, for 24 hours without causing a reaction.

A 4 per cent solution of formaldehyde can remain on the normal skin, in the form of a patch test, for 24 hours without causing a reaction.

Powdered hexamethylenetetramine may remain on the normal skin, in the form of a patch test, for 24 hours without causing a reaction.

Powdered coumaron resin may remain on the normal skin, in the form of a patch test, for 24 hours without causing a reaction.

Coumaron resin is used in varnishes, adhesives, rubber, paint, chewing gum, lacquers, paper and fabric sizing, printing inks, and waterproofing.

It is made from the crude coal tar distillate, which comes off between 150° and 200° C.

This distillate is re-distilled to remove impurities such as benzol, toluol, zylol, naphthalene and tar acids—and a sharply fractionated naphtha is obtained. The naphtha is dried in lead-lined or stone-ware receptacles by treatment with H_2SO_4, in the proportion of 3 to 5 parts per 1,000. After standing a while, the acid is drawn off and fresh H_2SO_4 is added slowly and agitated until 3 to 5 per cent of acid is added. The kettle is kept cold during the reaction with brine-cooled refrigeration.

After the reaction takes place, the mixture is allowed to stand until the tar and sludge settle. They are then removed and the remaining oil is pumped to a neutralizing tank and treated with caustic soda to destroy the remaining acid. The oil is then washed with water to remove the soluble matter, and it is allowed again to settle and the water is removed.

The oil is now distilled and the solvent naphtha is distilled off and the naphthalene is removed by live steam. After this, there remains a heavy oil boiling at 320°–330° C., which is removed from the resin.

COUMARON RESINS

There are no skin hazards, outside of acid and alkali burns, in these operations, because they are totally enclosed. No skin lesions were found in a large plant and the medical records for a number of years showed no cases of dermatitis.

Dermatitis has occurred from coumaron resin in varnish which was used on heddle frames in a cotton mill. The skin on the forearms of the weavers was struck continuously by the moving heddle frames and some developed dermatitis. Patch tests showed that they were sensitive to chlorinated ceresin and coumaron resin in the varnish. The varnish grades of coumaron resin, especially the darker resins, may contain sulphuric acids resulting from the sulphuric acid treatments, if they are not carefully prepared, and it is these acids that cause dermatitis.

SYNTHETIC WAXES

The principal synthetic waxes manufactured in this country are chloro naphthalenes and the chloro diphenyls. They are both used for practically the same purposes—as electric insulators on condensers, as insulators on electric wires, in paints, varnishes, and lacquers, and as oil in transformers.

The chlorinated naphthalenes are made by passing chlorine through

naphthalene and replacing of the hydrogen atoms with chlorine. One or more of the hydrogen atoms can be replaced, forming mono, di, tri, up to per chloro naphthalene, in which 8 of the hydrogen atoms are replaced with chlorine, the formula being $C_{10}Cl_8$. The more chlorine, the more solid is the material.

In making chlorinated diphenyls, it is first necessary to manufacture diphenyl, $C_{12}H_{10}$. This is manufactured by passing benzol, C_6H_6, through molten lead, at a temperature of about 800° F., where 2 molecules of benzol combine to form 1 molecule of diphenyl, hydrogen being set free.

Diphenyl is a solid, crystalline-like substance. This is melted in closed cylinders and chlorine is bubbled through, replacing the hydrogen. One or more of the hydrogen atoms can be replaced, forming mono chloro diphenyl, di chloro diphenyl, up to deca chloro diphenyl, $C_{12}Cl_{10}$. Hydrochloric acid is a by-product of this reaction. The chloro diphenyls are liquid or semi-solid, up to the hexa chloro diphenyl.

Nonochloro diphenyl, $C_{12}HCl_9$, sold under the trade name of Arachlor, is used as an insulator for automobile electric wires and in condensers, and also as a de-lusterer of rayon.

In the manufacture of the chloro diphenyls, the workers are exposed to a benzol hazard when the diphenyl is made, as well as to a hazard from the inhalation of the fumes of diphenyl.

The workers engaged in chlorinating the diphenyl, especially that part of the operation where the crude Arachlor is being re-distilled to remove impurities, are affected with an acne-like condition of the skin. This also occurs in workers exposed to the fumes of the chloro naphthalenes, or Halowax. The fumes of these compounds cause acne on the face and neck and may penetrate the clothes and cause acne-like lesions to develop on the covered parts, the shoulders, and the belt-line, and even on the penis. The lesions on the skin resemble acne. They begin as small, pale, elevated papules, many having no openings in them. They develop into hard cyst-like elevations under the skin, some of which go on to suppuration, forming boils. Some of the lesions also occur at the mouth of the follicles and resemble the comedones and pustules of acne vulgaris.

In addition to these skin lesions, symptoms of systemic poisoning have occurred among workers inhaling these fumes. Those working with the chloro diphenyls have complained of digestive disturbances, burning of the eyes, impotence and hematuria. The latter symptom developed among a number of men making amino diphenyl, which is used in the manufacture of a rubber antioxidant. Cases of death from yellow atrophy of the liver have been reported among workers exposed to the fumes of the chloro naphthalenes.

Patch tests performed with Halowax and with the chloro diphenyls have yielded negative results. The skin lesions probably result from the mechanical plugging up of the follicles of the skin with the waxes as the fumes solidify on the skin.* The chlorine present in the waxes may have an irritating effect on the plugged follicles and cause suppuration.

PREVENTION

1. The protection of the workers from the irritating chemicals that compose the resins and waxes from the resins and waxes themselves. To do this, the process should be totally enclosed. If this is not possible, hoods with suction exhaust should be so placed over open processes that dust and fumes are pulled away from the worker and out of the room.

*I have recently seen the wife and child of a worker who had developed comedones and pustules from contact with his work clothes which were saturated with halowax and which he was accustomed to wear at home. L. S.

2. The workrooms themselves should be ventilated by intake and exhaust fans to remove dust and fumes.

3. The floors, walls, and ceilings should be washed down at frequent intervals to keep them free of dust.

4. Two lockers should be furnished to each worker. One for his street clothes and one for his work clothes. The lockers for street clothes and work clothes should be in separate rooms, with the shower baths between the locker rooms. The worker coming to work enters the locker room for the street clothes, takes them off, and puts them in the locker and goes into the locker room where his clothes are kept and dons them. From this room he goes to the workrooms through a connecting door. At the end of his shift, he goes through this door to the work clothes locker room, takes off his work clothes and leaves them on the floor or bench to be washed and then goes to the shower baths and bathes and dries. Then he goes to the street clothes locker room, puts on his clothes and goes out of the door leading to the street. It has been estimated at one plant where such a system was instituted that 6 cents a day per worker will take care of furnishing clean work clothes each day.

5. New workers who are hypersensitive, but have only mild eruptions, should be given protective ointments and clothing and kept at work for about 3 or 4 weeks with the hope that they will develop an immunity or become "hardened." If this does not occur, they should be taken off the job.

6. New applicants for jobs should be carefully examined for skin diseases and those found to have them should not be employed.

7. There should be periodic medical examination of workers to detect cases of dermatitis and workers in chlorinated naphthalenes and diphenyls should be periodically examined for symptoms of systemic poisoning.

8. Laws should be passed making it compulsory for factories where there are skin hazards to adopt these measures.

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