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VINYL PLASTICS

Their Dermatological and Chemical Aspects

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DURING the past 12 years there has been a fivefold increase in the number of dermatoses caused by the chemicals used in the manufacture of plastics.¹ New plastics are being developed each year, and it is necessary that the industrial physician and dermatologist know the fundamentals of the chemistry of the different plastics, so that he will be able to judge correctly any case that comes to him for judgment concerning causal relationship with the work.

The patient knows little about his job except that he uses "raw stock" or "overlay" decorative, that he "spreads vinyl onto cloth" or that he "dips a plastic pencil into a solvent known as MEK." The examining physician should know what the chemical of the "raw stock" can be. He should know something about the chemistry of the vinyls and should have a speaking acquaintance with such things as MEK (methylethyl ketone), TCP (tricresyl phosphate), DOP (dioctyl phosphate), etc.

Plastics, in general, may be divided into five groups or classes:

1. Condensation
2. Vinyl (or polymerization)
3. Cellulose
4. Synthetic rubbers
5. Miscellaneous

Polymerization resins may be divided into six groups:

1. Polyvinyl resins
2. Polyacrylate resins
3. Polyvinylidene resins
4. Polyethylene resins
5. Polystyrene resins
6. Coumarone and indene resins

Polymerization is the chemical union of two or more molecules of a substance to form a new compound without the elimination of a secondary compound. A monomer is a substance consisting of a single part; a dimer is a substance consisting of two parts, etc.

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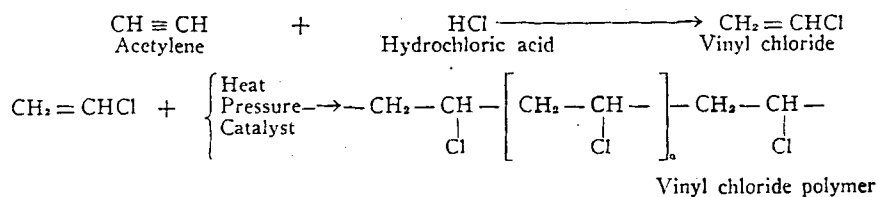
1. Morris, G. E.: Condensation Plastics: Their Dermatological and Chemical Aspects. *A. M. A. Arch. Ind. Hyg.* 5:37-43 (Jan.) 1952.

The polymerization resins are almost always compounded with other ingredients to produce the finished plastics. Compounding ingredients include plasticizers, stabilizers, pigments and dyes, lubricants, and fillers.

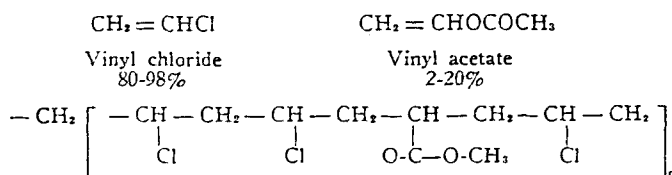
POLYVINYL RESINS²

Vinyl resins contain the vinyl linkage, $-\text{CH}_2=\text{CHX}$. X must be a strongly negative group—chloride, acetate, butyrate, alcohol, or acetal.

Vinyl chloride monomer



Copolymers



Dermatitis in a coater of vinyl plastics.

The more vinyl acetate that is used, the more soluble is the product and so the more useful for coatings (see "Flow Chart"). The trade names include Vinylite, Geon, Koroseal, Safflex, Marvinol, etc. They are used as moulding compounds, adhesives, fabrics, cable coverings, floor tile, belts, raincoats, toys, etc.

I have not seen any eruption from the finished product, but the Figure shows an eruption from vinyl latex used for coating artificial leather.

2. Shreve, R. N.: Chemical Process Industries, New York, McGraw-Hill Book Company, Inc., 1945.

Polyacrylate
derivatives:



Methyl Acrylate

$\text{CH}_2 = \text{CN} - \text{CH}$
Ethylene cyanoacrylate
The polymer

The trade name
coatings, leather
Only a few

Monomers

Polymerization

It is often
vinyl chloride

The trade name
covers, pipe,

Cracked pipe

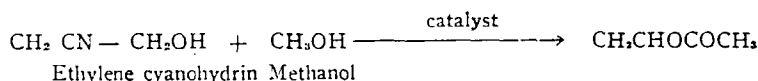
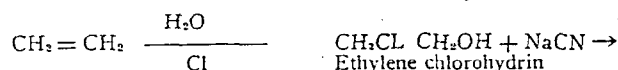
The trade name
of blown bottle
cable insulation

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Polyacrylate resins are formed from the polymerization of acrylic acid and its derivatives:



Petroleum $\xrightarrow{\text{Cracking process}}$ $\text{CH}_2 = \text{CH}_2$
Ethylene

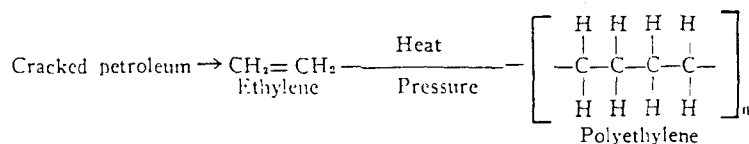

$$\begin{array}{ccccccc} -\text{CH}_2- & \text{CH}- & [\text{CH}_2- & \text{CH}]_n & -\text{CH}_2- & \text{CH} & \\ & | & & | & & | & \\ \text{O}=\text{C}- & \text{OCH}_3 & & \text{O}-\text{C}- & \text{OCH}_3 & \text{O}-\text{C}- & \text{OCH}_3 \end{array}$$

Only a few cases of stomatitis have been seen from acrylic dental plates.

Monomer—vinylidene chloride


$$\text{---CH}_2\text{---}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}\text{---}\left[\text{CH}_2\text{---}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}\text{---}\right]_n\text{CH}_2\text{---}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}\text{---}$$
$$\left[\begin{array}{cccccccccccc} \text{H} & \text{Cl} & \text{H} & \text{Cl} & \text{H} & \text{Cl} & \text{H} & \text{Cl} & \text{H} & \text{Cl} \\ | & | & | & | & | & | & | & | & | & | \\ -\text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{C}- \\ | & | & | & | & | & | & | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{Cl} & \text{H} & \text{Cl} & \text{H} & \text{Cl} & \text{H} & \text{H} \end{array} \right]_n$$

POLYETHYLENE RESINS

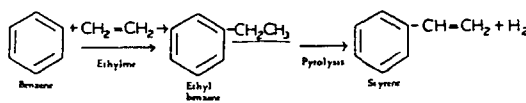
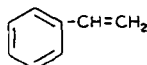


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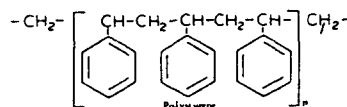
Occasional sensitization to these resins occurs, especially in workers coating the resins before complete polymerization has occurred.

Styrene

POLYSTYRENE RESINS



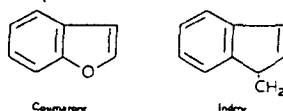
Polymerizes as follows:



The trade names are Lustron, Lustrex, Polystyrene, Styramic and Plexene. They are used as bottles, jars, closures, tableware, toilet articles, wall tile, brushes, etc.

COUMARONE AND INDENE RESINS

These are coal tar derivatives.



The polymerization is similar to that of styrene. The trade names are Cumar, Nevil-lac, and Nypene. These are used for coatings, varnishes, printing inks, tile, rubber compounding, and chewing gum.

The compounds added to the resins include plasticizers, stabilizers, lubricants, colorants and fillers.

Plasticizers are chemicals which render the finished product more plastic. They make up 10% to 50% of the weight of the finished product. They include the following: phosphates (tricresyl phosphate—TCP); phthalates (dioctyl phthalate—DOP); ricinoleic acid derivatives; sebacic acid derivatives; azelates; polyesters; nitrile rubbers; petroleum derivatives; chlorinated aromatic hydrocarbons.

Stabilizers are substances which prevent decomposition from heat and sunlight. They make up 2 to 5% by weight. They include lead compounds (basic white lead carbonate and basic white lead silicate); tin compounds, epoxides, phosphates, and metallic soaps.

Lubricants are added to plastics and make for ease of flow (internal and external). They include fatty acids, waxes, oils, and metallic soaps. The colors used include dyes and pigments.

Fillers are added to confer chemical resistance, mechanical strength, electrical properties, and thermal resistance. The mineral fillers are commonly used and include clays, mica, asbestos, limestone, and diatomaceous earth.

Vinyl r

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D may

CH₂ — Cl

CH₂—C—(C

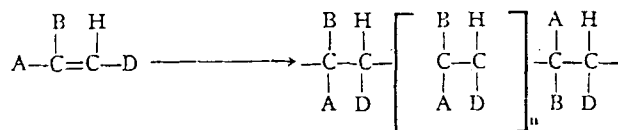
CH₂ CC
CH₂ CC

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SUMMARY

Vinyl resins are formed by the polymerization of



A and B are preferably hydrogen, occasionally Fl or Cl.

H may be hydrogen, Cl, F, CN, or CH₃.

D may be hydrogen or COOH, Cl, F, CN, COOR, C₆H₅, —O—R, —CH₃.

CH₂ — CH

H
C₆H₅
Cl
OR
O COCH₃
F
COOH
CN

Ethylene
Styrene
Vinyl chloride
Vinyl ether
Vinyl acetate
Vinyl fluoride
Acrylic acid
Acrylonitrile

CH₂—C—(CH₃)

COOH
COOCH₃

Methacrylic acid
Methyl methacrylate

CH₂ CCN
CH₂ CCl

CN
Cl
CN

Vinylidene cyanide
Vinylidene chloride
Chloroacrylonitrile

The polymerization resins are handled by enclosed processes until they are ready for shipment. Workers handling the partially polymerized resins may develop sensitization dermatitis. Eruptions caused by the finished products are rare but do occur.

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