Handling Procedures for DuPont Photopolymer Films

Technical Bulletin TB-9944

Introduction

This technical bulletin is an overview of the health and safety issues that may arise in the handling and processing of DuPont RISTON® and VACREL® photopolymer films. A number of concerns must be considered, including the photopolymer components that may affect health, their possible health effects, the means of exposure, and the control of these components in the workplace. Equipment and room ventilation requirements, key points in the control of these components, are also discussed in this bulletin.

Photopolymer films have been used in the printed wiring board (PWB) industry since 1968. During this time, safe handling and operating practices have been developed, resulting in a long and favorable safety experience. Specific deviations from these practices have been found to lead to health incidents. This bulletin is intended to help users understand the safety aspects of these products and to be aware of the health effects of the photopolymer film components. Once understood, the health and safety effects can be evaluated in routine use and possible routes of overexposure can be identified.

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Composition of Photopolymer Films

The components of a typical photopolymer film include: binders (polymers that act as film formers), acrylate monomers (that polymerize during exposure), photoinitiators (react with ultraviolet light, causing the monomers to polymerize), plasticizers (impart softness and flexibility), colorants (for film identification), adhesion promoters (improve film-to-copper adhesion), and chemical agents (for printout image).

Health Effects of Acrylates

DuPont as well as other manufacturers formulate photopolymer films with multifunctional acrylate monomers. Historical and toxicological information has shown that multifunctional acrylate monomers can produce potential health effects These effects can occur with both normal use conditions and with the variations anticipated, if the guidelines in this bulletin are not followed. Overexposure to the acrylates in the films can have these known effects:

- Respiratory irritation
- Skin irritation (dermatitis)
- Skin sensitization

Sources of Health Effects

Experience has shown that contact with photopolymer films through normal handling, such as threading the laminator with film or handling panels by their edges, is not a significant route of exposure. The multifunctional acrylate monomers are embedded in the films' polymeric matrix. *Casual contact does not appear to cause monomers to be transferred to the skin and absorbed in sufficient quantities to cause skin irritation.* It should be noted, however, that human sensitivity to chemicals varies. Always follow good industrial hygiene practices when handling these films.

Incidence of Health Effects

Numerous operators worldwide have handled DuPont photopolymer films daily for forty years, but DuPont has received only a few inquiries per year on health effects. Although not every instance of related health effects is reported, the records show that few cases occur.

Respiratory Effects

Heating of photopolymer films generates vapors that contain acrylate monomers. Experience has shown that exposure to these vapors, and to condensate resulting from these vapors, is responsible for virtually all reported health effects. To prevent exposure, equipment that heats the film must have an exhaust system that will remove vapors from the workplace and avoid the formulation of vapor condensate.

Inhaling vapors from heated film may result in dryness and irritation of the respiratory tract. This is especially true if films are heated above their normal use temperature. More harmful effects are possible if normal safety precautions (e.g., laminator ventilation) are totally disregarded.

Skin Effects

The incidence of dermatitis resulting from exposure to the acrylates in dry photopolymer film is very low. Skin exposure to a sufficient amount of acrylates in either liquid condensate or vapor form, may cause redness and itching of the affected skin area; there also may be slight blistering. The condition looks very similar to poison ivy, (Rhus toxicodendron), and is often diagnosed as such. The degree of reaction varies with the amount of exposure and the sensitivity of the individual; some persons will be unaffected by any contact. If dermatitis effects occur, determining the source of the exposure and implementing the required engineering controls should be given top priority.

Sensitization

Skin sensitization occurs when the body shows an allergic response to a substance, usually triggered by exposure to a much smaller quantity of the material than is necessary to cause dermatitis. Some persons may develop sensitization over a period of time. A typical sensitized response to acrylates is swelling of the face, typically around the eyes, often nearly closing them. DuPont is not aware of any more serious or life-threatening effects.

Persons exhibiting sensitization symptoms should be referred to a physician. Sensitized persons may have to be reassigned to a job that does not involve exposure to acrylates.

NOTE: Other chemicals used in PWB fabrication can also be skin or respiratory irritants and must be considered. Epoxy materials, for example, are recognized as sensitizers.

Routes Of Exposure To Acrylates

There are several places in the process where there is potential for exposure to acrylates. With RISTON® films, it is likely to be the vapors and condensate around the heated roll laminator. With VACREL films, it is most likely to be the vapors liberated during oven curing. There is also a potential for exposure from contact with developer solutions in which these films are dissolved. While handling of the film and its coversheets has not been shown to be a significant route of exposure, it should be considered in any health evaluation, especially if repetitive contact occurs.

Contact with Vapors and Condensate

Laminators

Vapors containing acrylate monomers are emitted when the film is in contact with the heated rolls during lamination. Therefore, the areas closest to the roll will have the highest vapor concentrations. Vapors that are allowed to escape may condense on relatively cool surfaces nearby, such as metal parts of the laminator or even the operators hands and face. The vapor condensate is an oily liquid that contains higher concentrations of acrylate monomer that the vapors. It can be easily picked up, spread, and absorbed by the skin. If an oily liquid appears on or around the laminator, it is likely to be condensate and should be removed as soon as possible. Wear neoprene or nitrile gloves and use a disposable towel moistened (not wet) with isopropyl alcohol to remove the condensate. *Handling Contaminated Clothing* in this bulletin provides safe handling guidelines for contaminated gloves and clothing.

WARNING!

Isopropyl alcohol is flammable. Keep wet cleaning materials away from hot surfaces and electrical contacts such as switches.

Safe operation requires that the vapors be removed at the point of generation by an efficient exhaust system. DuPont laminators have been designed and tested to assure safe operation. The exhaust on other laminator designs should be checked for adequacy.

When DuPont laminators are installed and operated according to published instructions, including the guidelines in this bulletin, the measured airborne concentrations of total organics in the operator breathing zones have been less than one part per million (ppm) for RISTON® and VACREL® films.

Check the exhaust system for proper flow rate to avoid further condensate accumulation. If the exhaust duct must be cleaned, or if it contains a condensate trap that must be drained, wear neoprene or nitrile gloves and appropriate protective equipment to avoid skin contact. Keep the exhaust ventilation operating during cleaning. Small amounts of condensate can be disposed of in the sump of a loaded developer unit.

Preventive Recommendations

While direct contact with the film is not an expected or typical route of exposure (based on field experience), good industrial hygiene practices should be followed to avoid even a remote chance of exposure to monomers. For that reason we offer the following recommendations concerning handling photopolymer films.

- Be certain that the laminator exhaust system meets the design and flow recommendations of the equipment manufacturer. Table 1 lists the recommendations for DuPont laminators.

- Wear neoprene or nitrile gloves and wipe off the surfaces adjacent to the heated rolls at least once a day, or once a shift with heavy use. Use a disposable towel moistened (not wet) with isopropyl alcohol. Since the towels will pick up monomers, discard them promptly and carefully.

- Instruct operators to periodically wash their hands with soap and water during a shift. Operators should routinely wash their hands at the end of a shift and before smoking, eating, or using toilets. If skin is directly exposed to condensate or developer, wash the skin area within a few minutes of contact. Careful washing with soap and water is most effective in all circumstances, but it must be done promptly. Washing within five minutes of contact is effective, even for a sensitized person. If soap and water is not immediately available, the use of pre-moistened wipes may be acceptable until soap and water can be used.

- Discourage operators from wearing watches and rings. In addition to being safety hazards around operating equipment, jewelry can trap film vapors and condensate against the skin. The monomers may not be removed adequately during routine washing while jewelry is worn.

- Instruct operators to be careful about using and maintaining protective clothing. Lab coats should be laundered at least once per week. Nylon fabric gloves used by operators should be changed twice per shift to avoid buildup of dirt and contaminants. Gloves should not be turned inside out or used until they look dirty; they should be laundered or discarded after each use.

- Maintenance personnel working on the laminator, or its immediate or downstream exhaust system, should be fully informed about the hazards of the condensate and should be required to wear suitable protective equipment; neoprene or nitrile gloves and safety glasses are the minimum. Gloves should be decontaminated or discarded after each use.

Contact with Curing Oven Vapors

After the PWBs laminated with VACREL® film have been exposed, developed, they are UV and thermally cured. The ovens used for this process must be connected to a plant exhaust system to ventilate any outgassed materials. DuPont recommends a dilution rate of 2.5 cfm for every 100 mil-sq. ft. of cured film.

Do not open oven doors during the curing cycle. When curing is completed, turn off the recirculating air blower before opening the door and removing the boards. Some users open the oven door slightly for five to ten minutes with the exhaust operating to cool the panels and avoid fumes entering the room. (See DuPont publication number E-52159, *Handling and Safety Considerations for the VACREL Solder Mask Curing Process*.)

Contact with the Film

Photopolymer film resists are produced between a layer of MYLAR® , polyester film and a layer of polyolefin film. The polyolefin film is removed during the lamination step. The MYLAR® film remains as a protective coversheet until the development step. Since the coversheet is in place during most board handling, there is minimum opportunity for direct contact with the photopolymer film. However, constant and prolonged contact would increase the likelihood of skin irritation.

Direct contact may occur during laminator thread-up when the polyolefin film is separated from the photopolymer film and its polyester coversheet. The film and coversheet are then threaded through the laminating rolls; details are given in the laminator instruction manuals. Care should be taken to avoid or minimize contact with the unprotected side of the dry film. The normal thread-up time for an experienced operator is usually less than one minute.

Since the film is photo-printed with the polyester coversheet in place, there is little, it any, chance of film contact during UV exposure.

Another source of direct contact is when the polyester coversheet is removed just before the panels are developed. Operators should avoid skin contact with the film during coversheet removal. They should also use caution when disposing of the coversheets since they may contain small amounts of residue.

Avoiding Film Contact

1. Operators on the output side of manual laminators, such as the DuPont HRL, trim the excess film from the panels exiting the laminator. They should be made aware of the hazards and encouraged to minimize contact with the film scraps. A trash can positioned under the exit table will allow operators to easily discard the film scraps.

   The polyolefin film that is removed during lamination is wound onto take-up rolls. This film is likely to contain small amounts of monomer and must be appropriately recycled or discarded.

2. When feeding the developer, operators often lay large panels on their forearms. Operators should wear long-sleeved lab coats. Use lightweight, long-sleeved lab coats and latex gloves to avoid skin contact. Use lightweight lab coats in warm areas to minimize perspiration. Moist skin is more likely to leach monomers out of film than dry skin.

   Operators who feed or remove panels from the developer should handle the panels by the edges only.

3. Operators should minimize contact with the used polyester coversheets. They should not attempt to ball or crumble them for disposal. This film is likely to contain small amounts of monomer and must be appropriately recycled or discarded.
4. The polyolefin film, the polyester film coversheets, and

all photopolymer film scraps should be placed into trash cans lined with plastic trash bags. The trash cans and bags should be open enough to allow easy disposal of coversheets without having to ball or fold them.

Static electricity may cause the cover sheet film to cling to the plastic liner. Use a stick or similar device to tamp the film into the bag to avoid skin contact.

Avoiding Contact with Developer

Loaded developer is a solution of the film components. The monomer is likely to cause dermatitis if skin is wet with the developer solution, or if clothing is wet with developer and remains in contact with the skin. Rubber gloves that operators may wear when handling loaded developer should be changed and washed after exposure to the solution.

Safe Laminator Operation

Primary Imaging Laminators

Laminators for RISTON® photopolymer films are threaded so that the polyolefin film layer is removed just before lamination. The MYLAR® film coversheet side of the photopolymer film then contacts a 90- to 110-degree radius of the laminating roll, heated roll, heating the photopolymer film. This is the area where vapors are generated and where ventilation is critical. As the film enters the roll nip, it is sealed to the boards or to itself. The polyester film coversheet becomes an effective vapor barrier, so there is no problem with vapor contact after lamination.

The following information is specific to DuPont laminators. Also, refer to *Laminator Exhaust Check* in this bulletin for general information.

Hot Roll Laminator

DuPont HRL laminators and LC-2400 cleaner units have integral exhaust systems to remove vapors effectively. However, these systems must be checked and cleaned routinely to ensure unrestricted air flow. Low air flow will result in vapors escaping into the area and condensate formation. On LC-2400 units, be certain to check the drive belt for the built-in exhaust blower and the condition of the vent hoses.

Cut Sheet Laminators

The film cutting and laminating areas of cut sheet laminators, such as the Hakuto CSL and the DuPont ASL are usually enclosed. Removable covers are used where access to the film and equipment is needed. An exhaust vent connection near the top of the laminator cabinet provides a path for the resist vapors to be drawn out of the laminator cabinet by an external exhaust system.

Since the exhaust vent connection is not close to the heated rolls, high air flow rates are needed for proper exhausting of the outgassed materials. Efficient vapor removal also requires that all covers remain in place during operation.
Take steps to minimize contact with the heated resist during thread-up and normal maintenance operations.

Solder Mask Laminators

In the DuPont Vacuum Laminators (SMVLs), the VACREL® photopolymer film solder mask is heated by platens inside the vacuum chamber. The solder mask film is laminated to the panel in a sealed chamber. After lamination, the MYLAR® film coversheet acts as an effective vapor barrier.
Essentially all of the vapors that are produced in the vacuum chamber are removed through the vacuum pump. The pump needs to be exhausted to a plant system, although only minimal flow and negative pressure is required in the vent.

Use caution when changing the vacuum pump oil. The pump oil will absorb outgassing components from the film and may contain condensate from the vent duct.

Care also must be taken when replacing the vacuum hoses and servicing the vacuum solenoid valves. These components may contain condensate from the film vapors.

Hot Knife trimming and Burning-out of Tooling Holes

Use of heated knives or soldering gun tips to trim photopolymer films will generate vapors that can be irritating. These vapors will follow air currents and disperse in the room. A specially designed exhaust system is required to remove the vapors at the point of generation.

Using heated tips to burnout tooling holes presents a similar situation to trimming with heated devices. To avoid problems, some users have designed special tables with through-holes that align with the tooling holes in the panels. Exhaust air is

drawn through the holes in the table to remove vapors at each tooling hole. Minimal exhaust flow is required with this design.

Laminator Exhaust Check

When troubleshooting a dermatitis problem that may be caused by inadequate laminator exhaust, be certain that the exhaust system meets the design and flow recommendations of DuPont or other equipment manufacturer. Also, check the following:

1. Is the exhaust system on? If there is no air flow in the duct to the laminator, check at the source (internal blower or plant system).

   Some exhaust systems are improperly terminated into a false cailing area rather than being connected to the plant system or vented outdoors.

   If flexible hose is used for the exhaust duct, condensate may have attacked the material and collapsed the inner walls; only rigid PVC pipe should be used for laminator exhaust vents.

2. Is there any air disturbance around the laminator? The air from a fan, air circulator, air inlet vent, or even a frequently opened nearby door can interfere with the exhaust process. A smoke tube can be used to check for drafts and other interference with the intake of the air into the exhaust system.

3. Has equipment been added in the shop since the original exhaust system was installed? The exhaust from other equipment may have made the laminator exhaust inefficient or ineffective.

   Vapor problems can occur when two or more laminators with built-ins blowers, such as the DuPont HRL with an LC-2400 cleaner, are used with a common exhaust duct. If the exhaust system is not carefully designed, vapors from an operating laminator can enter the room through the exhaust vent of a nonoperating laminator. Provisions must be made to prevent this occurrence.

Check the laminator exhaust rate with an anemometer every six months to ensure that it meets the specifications. Specifications for DuPont laminators are given in Table 1. Anemometers are relatively inexpensive and are often needed for measurements required by OSHA. (Plant or contractor heating and ventilating personnel usually have these devices.)

Place an inspection tag on the exhaust vent to record the flow rate and date of each check. If the air flow rate falls below the specified velocity, notify the proper person to take corrective steps.

Handling Contaminated Clothing

Removal and handling of contaminated protective clothing must be done with caution. Remove disposable gloves by pulling them inside out from the wrist area, avoiding any skin contact. Reusable gloves should be thoroughly decontaminated *before removal* by washing them with soap and water.
Launder arm sleeves, lab coats, and other protective clothing frequently, at least once per week.

If clothing or shoes become wet with vapor condensate or used developer, they should be removed promptly and laundered. Avoid contact with the outside surfaces as much as possible.

Wash hands with soap and water after handling contaminated clothing and before smoking, eating, or using toilets.

Yellow Room Environment

Yellow rooms that are crowded with operators and equipment tend to be warm and often have insufficient air movement. These conditions may lead to operator complaints. Rooms should be airy, free of congestion, have good work flow, and adequate fresh air circulation. DuPont recommends that yellow room ventilation systems be designed for six air changes per hour, with minimum of 10% fresh air. Be certain to recheck the room ventilation when the HVAC system is switched from heating to cooling and vice versa.

Situations have also been identified where the overall room ventilation is good, but isolated pockets of stagnant air has led to operator complaints. This is typically caused by the placement of equipment and large racks of panels, or low ceiling in part of the room that restricts the flow of the room air circulation.

A good reference book on this subject is *Industrial Ventilation*, available from:

American Conference of
Governmental Industrial Hygienists
6500 Glenway Ave., Bldg.D-7
Cincinnati, OH 45211 U.S.A.
This book is updated every two years; order the most current edition.

Film Odor

Shop personnel often associate film odors with health hazards. However, the odors primarily come from trace impurities in the film, not from its components. It has been shown that there is no relationship between a chemical's odor and its toxicity.

Low molecular weight acrylates are known trace impurities in photopolymer films. The concentrations where the odor of these acrylates can be perceived and recognized may be hundreds to thousands times lower than the level that is recognized as acceptable for a safe working environment.

The Odor Index ia a way of assessing a material's odor potential. This index is a dimensionless term equal to the vapor pressure of a substance divided by the odor recognition threshold in parts per million (ppm), as determined by 100% of a panel of human subjects. The vapor pressure represents the ability of a material to disperse into the air. The recognition threshold is a measure of the detectability of that substance. Therefore, the higher the vapor pressure and the lower the threshold, the more likely that the substance will be detected and be perceived as a problem in the workplace.

Note that the Odor Indexes does not differentiate between pleasant and unpleasant odors. The indexes of several materials that are common in photopolymer films and the PWB industry are given in Table 2. As shown, some materials can be detected by smell far below any level that might be considered dangerous. Be certain to follow the recommendations for room air ventilation to minimize complaints about odors and provide a pleasant working environment for employees.

Differences In Odor Characteristics

The trace volatiles that contribute to a film's odor are somewhat different for the various photopolymer film types. While all DuPont films possess a typical sweet acrylate characteristic, the exact odor is different for each film type. Experience has shown that operators quickly become used to and accept the odor of a particular film or group of films. However, they often respond negatively when a film with a different odor is introduced[1]. If complaints are received in such circumstances, check the laminator exhaust and the room air ventilation before reassuring the operators that no additional hazard exists.

Table 1. DuPont Laminator Exhaust Recommendations

Laminator Type	Exhaust Flow Rate M^3/min (cfm)	Connection Dia. Min(in)	Exhaust Location
HRL-24	1.7 (60	76 (3)	At Roll Nip
HRL-24/LC-2400			
High Speed	8.5 (300)	102 (4)	At Roll Nip
Low Speed	3.7 (130)		
ASL-24	8.5 (300)	76 mm (3)	Chimney Cabinet
SMVL-100/300 Series	Negative Pressure only	Pump outlet fitting	Vacuum Pump

Table 2. Typical Odor Index and 100% Odor Recognition Concentrations

	Odor Index	100% Recognition Treshold (ppm)	PEL or TLV 8 hr TWA (ppm)
Reference Material			
Acetic Acid (vinegar)	15,000	2	10
Acetone (nail polish remover)	720	300	500
Isopropyl Alcohol (rubbing alcohol)	60	200	400
Isopropyl Mercaptan (odor added to natural gas)	1,052,000,000	0.2(ppb*)	10
Substances in Photopolymer Film or PWB Chemistry			
Acrylic Acid	105,700	1.04	2
Butyl Acrylate	525,000	20 (ppb*)	10
Butyl Cellosolve	1,650	0.48	25
Ethanolamine	130	5	3
Ethyl Acrylate	38,160,000	0.3 (ppb*)	5
Formaldehyde	5,000,000	1	.75
Methyl Alcohol	22	6,000	200
Methyl Alcohol	22	6,000	200
Methylene Chloride	2,100	50-300	50
Methyl Methacrylate	119,705	0.2	100

* Parts per billion

NOTES: For comparisons between materials, it is suggested that values be placed in one of three categories.

1. High odor potential: Odor Index >1,000,000
2. Medium odor potential: Odor Index 100,000 - 1,000,000
3. Low odor potential: Odor Index <100,000

Exposure limits are accurate at the date of publication, but will not be updated regularly.

Odor data and information is summarized from the *Handbook of Environmental Data on Organic Chemicals*, by K. Verschueren (Van Nostrand - 1983). PEL and TLV data as of 1999

[1]Reference: *Odors from Stationary and Mobile Sources*, National Academy of Sciences, Washington, DC. (1979)

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