

Do you work with ISOCYANATES and POLYURETHANE?

WARNING!
New risks
identified!



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Introduction

The dangers of isocyanates have been known for many years. What we have not been aware of is that the measuring methods used do not detect all the isocyanates that may occur. With new measuring methods, we hope to find answers as to why some people whose work involves heating polyurethane, PUR, mineral wool and some types of Bakelite suffer acute symptoms and in the most severe cases even asthma.

In light of the fact that heating these products occur in various situations in working life, it is essential that thorough information about the risks be made available. Such information is particularly important to the employer – who bears the main responsibility for the working environment – but also to others: union representatives, supervisors and company health care personnel, all of whom assist the employer in various ways e.g. through performing exposure measurements and implementing preventive action.

This report is based on a series of information brochures produced by the Joint Industrial Safety Council on the initiative of the employer and union organisations concerned and directed towards workplaces in Sweden. Information brochures have been produced for eight different industries or risk areas. The information is also available on the Internet.

PUR is being used in an increasing number of environments and in all countries. The risk of exposure to isocyanates is the same. We should therefore like to share our experience and call upon everybody to analyse their own risks, to be more alert and to play their part in active prevention in order to reduce the problems and suffering for all those who work with isocyanates.

JOINT INDUSTRIAL SAFETY COUNCIL
Ingvar Söderström/Managing director
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New risks!

In recent years in Sweden, new hazards have been found to be associated with certain chemical products and with plastic/rubber materials that are manufactured with isocyanates and which contain PUR (polyurethane). These risks were discovered by measuring with a new and improved method. This may also occur with binding agents in mineral wool or in some types of the plastic Bakelite. When PUR is heated, toxic compounds are produced – isocyanates – which can harm the respiratory system. When heating plastics and resins made from urea and phenol or formaldehyde (which does not contain PUR) an isocyanate (methyl isocyanate) can be formed. The levels may be high, so high that they cause asthma. Measurements made in the past with old methods have almost always shown low levels of isocyanates. New measuring methods show that the levels can be very high. The reason is that the old methods do not detect all the different isocyanates that can be generated when materials containing PUR are heated.

High levels of isocyanates can cause asthma. There are suspicions, moreover, that the respiratory system can be affected by very short-term exposures to high concentrations. In the worst-case scenario, a few breaths of smoke from something containing PUR can be sufficient to harm the airways.

When materials containing PUR are heated, e.g. in heat treatment, welding, torch-cutting, sawing, cross-cutting, grinding or soldering, or when heating material in some other way, a large number of different compounds are formed. These include isocyanates. It is sufficient for the temperature to become high at a single point for isocyanates to be formed. It is estimated that breakdown can begin at about 150–200° C and sometimes at higher temperatures. Isocyanates are odourless, but sometimes other substances are formed which

do have an odour. If polyurethane plastic is heated to the point of discoloration, isocyanates are formed – but the plastic may also be emitting isocyanates even before discoloration occurs.

Do you know if there are any isocyanates in the chemical products that you work with, e.g.:

- paints and varnishes, e.g. two-component and hardening types, and those that are intended to be durable, including water-based paints.
- surface treatment (coating)
- adhesive, particularly hardening adhesive and adhesive designed to withstand high stresses.
- joint sealing compound
- joint sealing foam
- underseal compound for vehicles
- filler
- raw materials for foam plastic
- raw materials for foam insulation
- raw materials for urethane rubber
- resin for cold-box moulding
- sealing compound for concrete cracks?

Do you know if polyurethane (PUR) or plastics and resins made from urea, phenol or formaldehyde, e.g. "urea resin" are to be found in the materials you work with, e.g. in:

- painted materials, e.g. body work of vehicles and other items treated to withstand stress
- varnished materials, e.g. circuit boards and other items treated to withstand stress

- surface treatments (coating), e.g. on copper wire and optical cables (the latter may also have a casing of foam plastic)
- bonded materials, e.g. vehicle windows, wallpaper for bathrooms, etc., and structures that require strongly bonded joints that can withstand stress, e.g. in metal, plastic or wood
- filler, e.g. filler for use in vehicles
- sealed concrete
- soft or rigid foam plastic
- foam insulation, e.g. as insulation or protection around pipes, copper thread or cables
- urethane rubber
- underseal compound for vehicles or joint sealing compound or joint sealing foam
- resin for cold and hot-box moulding
- binding agents (containing resins made from urea and phenol or formaldehyde), used in certain types of mineral wool (glass, rock and slag wool) and sometimes in glass fibre?
- plastics made from urea and phenol or formaldehyde, e.g. some types of Bakelite.



Do you ever work with materials that may contain polyurethane (PUR) or plastics and resins made from urea and phenol or formaldehyde in such a way that the material is heated, e.g.:

- heat treatment with heat gun, e.g. flame or hot air
- welding
- soldering
- cutting (with cutting torches or hot wire)
- saws, cross-cutters or grinders
- moulding using the cold or hot-box method
- heats up mineral wool that is used as insulation?

It is not just the visible part of the material that can be heated. Sometimes there is material on the rear of or inside a structure, e.g. underseal compound behind a car panel, a adhesive joint or foam insulation inside a technical structure or in a wall.

How do you know if you are working with isocyanates or PUR?

In order to find out if isocyanates are used in the materials you are working with, you must have access to safety data sheets. Those who use a product often have access to safety data sheets, but those who process a finished adhesive joint, or plastic, painted or varnished product, etc., rarely do. Ask for information from the company that has manufactured or processed the product, e.g. painted it. The types of product listed on page 2 may contain isocyanates if they are manufactured or processed after 1960. Products containing isocyanates/polyurethane are often used in environments where they must withstand high levels of stress, e.g. heavy loads wear or aggressive chemicals.

- Assume that all **foam plastic** (except expanded polystyrene) contains PUR. Expanded polystyrene is a common rigid foam plastic that **does not** contain polyurethane. Flexible foam plastic is used in vehicle interiors, mattresses and padded furniture, for example, and rigid PUR foam plastic is used as insulation in refrigerators, freezers, district heating pipes, vehicles and buildings, e.g. as joint sealing foam, foam pipe insulation and foam insulation in walls. Expect all foam plastic (except expanded polystyrene) to emit isocyanates when heated.
- **PUR adhesive** may be found in single and two-component adhesive, water and solvent based adhesive and hot-melt adhesive, particularly in joints that must be strong and durable.
- **PUR paint and varnish** may be one or two-component, powder or water-based, and is found particularly in paints and varnishes that are designed to withstand strong wear and to be resistant to chemicals. PUR paint is often used for factory-painted metals.

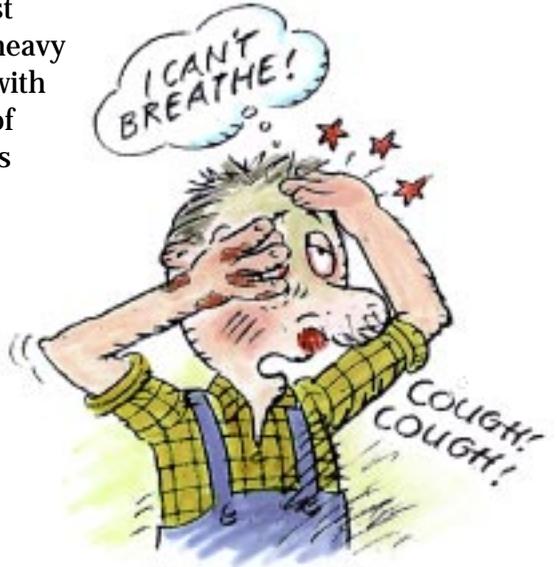
- **The coating** on optical cables is normally an acrylate varnish that contains small amounts of PUR.
- **Sealing compound** for cracks in concrete may contain PUR.

In the EU, directive **91/155/EEG** applies. This specifies the information to be shown on **safety data sheets**. Compounds hazardous to health are to be listed under **heading 2** of the safety data sheet. If the concentration of isocyanates exceeds 1% (the limit is 0.5% for certain isocyanates and 0.1% for TDI and soon also for MDI) this must also be shown under heading 2. If the product contains less than 1% (0.5% or 0.1%) isocyanates, no specification is required, but certain suppliers state it anyway. If for instance, it says "isocyanates" (often preceded by something, such as toluene di-isocyanate), TDI, MDI, HDI, IPDI, NDI, DIFPI (common abbreviations for various isocyanates) then the product contains isocyanates. A product that contains isocyanates (even if the levels are below 1, 0.5 or 0.1% respectively) must carry the following text on the packaging: "Contains isocyanates. See information from manufacturer".

When heated, certain products can emit dangerous amounts of isocyanates even if this is not made clear under heading 2. This applies particularly to products containing prepolymerised isocyanates or PUR polymers (polyurethane is sometimes stated as a polyester or polyether). The supplier must also issue a warning in the safety data sheet that isocyanates may be generated in conjunction with welding or heating, but this is not always the case (see under **headings 10 or 16**). There is no certainty that the safety data sheet contains the information you require, so there is good reason to check the data.

Might I become ill?

Isocyanates can give rise to a range of symptoms. The most usual ones consist of respiratory problems, e.g. nasal congestion, runny nose, dry cough or nose bleeding. Diffuse symptoms such as eye irritation, headaches or feeling heavy-headed also occur. Lung function may be impaired, which is most noticeable in the form of heavy breathing in conjunction with physical exertion or loss of stamina. It may sometimes be difficult to identify impaired lung function oneself, but a doctor can measure it. The symptoms may arise at work, but they may also only be noticeable several hours after work. They usually disappear after a few days away from work.



Severe cases may involve asthma, which is life-long. Every time one is exposed to isocyanates one can suffer an asthma attack. Asthma may also mean that the airways become more sensitive to dust and odours. This means that an asthma attack can be triggered by such things as perfume, exhaust emissions or solvents.

Isocyanates can also cause contact dermatitis.

Conditions involving the above symptoms, particularly asthma, can – in the EU at least – be registered as occupational injuries if they can be linked with exposure to isocyanates.

Have you had a medical examination?

Certain countries require medical examinations of personnel who may have been exposed to isocyanates when materials containing PUR have been heated. Although this is not the case in every country, it is worth recommending for preventive purposes. A medical examination should be carried out before work begins. This applies both to the person involved in the hot work itself and those in the vicinity, where there is a risk of isocyanates being spread. The examination includes an assessment of whether a person runs an elevated risk of illness as a result of hot work with PUR and whether he or she should therefore not carry out such work. The employer is responsible for this being done and should also maintain a register of persons who have undergone medical examination. See also **EU directive 98/24/EG, Article 10**, Health examinations, and any national regulations.

How can I protect myself?

Proceed as follows:

- ▲ Find out if the products you come into contact with contain isocyanates. If you are unable to find out with certainty, assume that raw materials, especially in foam plastic, foam insulation, joint sealing compound, sealing compound for cracks in concrete, underseal compound and filler for vehicles, and non-hardened adhesive, paint, varnish and coating that shall withstand substantial stresses may contain isocyanates. Isocyanates also occur in cold-box moulding.
- ▲ Find out if it is possible to switch to other products that do not contain isocyanates or PUR. If this can be done, there is no need to adopt potentially troublesome and expensive safeguards.

An example:

- A company that manufactures rail and underground railway wagons has replaced its polyurethane adhesive for the windows with an MS adhesive.



PUR adhesive has been replaced by an MS adhesive (a Simson adhesive). The bonding process is the same as before, but no protective equipment is required and the process can be carried out even with other people working close by. This makes the bonding process more flexible – in the past, it was only possible to do it at nights and weekends.

- ▲ there are adhesives, paints, varnishes and underseal compounds that do not contain isocyanates/PUR. Perhaps one of them meets your technical needs.

If the materials you work with are heated to 150° C or above, find out if they contain or may contain PUR or plastics and resins made from urea and phenol or formaldehyde, e.g. products that are painted, varnished or bonded and are intended for high stresses, copper wire or optical cables, joint sealing compound, joint sealing foam, underseal compounds, filler, foam plastic, foam insulation, urethane rubber, resin for hot and cold-box moulding or sealing compound for concrete. If you cannot be certain whether or not the materials contain PUR or plastics and resins made from urea and phenol or formaldehyde, assume that they can emit isocyanates when heated.

- ▲ if a product containing PUR must be used, avoid heating it to more than 150° C. This also applies to occasional jobs such as repair and maintenance and when dealing with spillage.

Some examples:

- instead of cutting with a disc, use a nibbler or sabre saw
- use pipe cutters instead of disc to cut thin pipes with foam insulation
- do not remove spillage containing PUR or isocyanates by heating with a heat gun. Scrape or cut instead
- peel the coating off optical cables mechanically with special equipment instead of using heat to remove it
- scrape away paint, adhesive, plastic etc before work starts so that the materials that can emit isocyanates are completely removed before heating. Everything must be removed. Any residues will form isocyanates.



In order to avoid poisonous gases, the layer of paint and isolating foam should be completely removed by at least 25 cm on each side of the welding place.

- ▲ If a material containing PUR that cannot be replaced is heated to 150° C or more, ensure that the workplace has proper ventilation. This means that all the smoke and vapours must be extracted. A permanent workplace that is encapsulated or screened and has the extractor directly above the product to be heated (warm smoke and vapours rise) is usually best. An adjustable welding smoke extractor or a welding gun with an extractor is not a good solution. Some smoke will always escape extractors of this sort. Some examples:
 - repair of circuit boards, which often involves soldering on varnished cards, can be done in a well-ventilated box that effectively takes care of the smoke formed, *see illustration*.



This company repairs circuit boards. An extractor cabinet has been built for soldering and other jobs in which isocyanates are generated. It was designed by the staff together with a consultant in order to ensure its suitability for the various jobs involved. When the extractor cabinet is in use, no protective equipment is required. There are no measurable levels of isocyanates outside the cabinet.



- work on body work of vehicles involving welding or grinding, for example, can be performed in a screened and well-ventilated room at reduced pressure. The person working in the room must carry breathing equipment, but no isocyanates are spread to those working elsewhere in the workshop, *see illustration*.
- ▲ If these measures are inadequate, personal protective equipment must be used. The safest method is the compressed-air face mask. This must be worn throughout work and not removed until the vapours have been extracted. The levels of isocyanates are often elevated for quite some time after work has been completed. For isocyanates formed in conjunction with heating, filter masks with a combination of carbon and particle filters provide some but inadequate protection. Work is under way to develop filter masks to provide protection against the isocyanates generated in conjunction with the heating of PUR.
- ▲ In order to prevent isocyanates being spread to other workplaces, the PUR material must be heated in a well ventilated, separate room at reduced pressure. Maintenance and repair personnel and others who carry out occasional jobs should be informed of the risks involved in heating materials containing PUR, as well as of the safeguards that should be observed in the work area.



A mobile booth for work involving isocyanates has been developed at this company. The booth can be moved around among ten workstations and is connected to a ventilation system that is fitted at each workstation. The mobile booth means that isocyanate work in progress does not disturb the people working alongside. Those working with isocyanates in the booth must wear a compressed-air face mask.



Should concentrations in the air be measured?

Sometimes it is a good idea to measure the concentrations of isocyanates in the air, particularly at fixed workstations where the jobs are always the same. One can, for example, perform measurements to:

- determine if safeguards yield good results. In such cases it may be necessary to measure both before and afterwards;
- determine whether PUR exists in a given product or not, if there is any uncertainty. It may be simpler to take measurements than to implement safeguards simply because isocyanates may be generated. One can also send in material samples in order to find out if it contains PUR – analysis of samples is much simpler and less expensive than measurement of concentrations in the air;

- determine exposure levels of isocyanates if somebody has shown symptoms in conjunction with work. If the levels are above or close to the limit value, action must always be taken to reduce the level of isocyanates, regardless of whether or not any symptoms have been observed. Biological measurements, which involve checking levels of isocyanates in the blood of persons who may have been exposed, may also be helpful in certain cases.

When interpreting measuring results, it is important to consider that the levels of isocyanates may vary at one and the same workplace. They may be either higher or lower than at the time the measurement was taken.

When measurements are carried out, avoid the old "MAMA" method and the "2-MP" method if the isocyanates are formed in conjunction with heating or if you do not know exactly which isocyanates occur. It has been found that these methods do not work well in conjunction with heating. Use the **DBA method** instead (or the new methods that are under development. These measure several types of isocyanate, as well as other substances such as amines which are formed when PUR is heated. As a supplement, it can be worth using instruments that indicate short-term peaks, but which do provide a quantitative measurement. Such peaks can not be measured with the DBA method. Contact the person responsible for the working environment at your workplace. He or she can engage an expert in occupational hygiene measurements. See also **EU directive 98/24/EG, Article 6**, Special safeguards and preventive action.

Have you received any training?

Those who work with products containing isocyanates or who may be exposed to isocyanates formed as a result of thermal breakdown must receive training about the risks involved in their work. This is regulated in **EU directive 98/24/EG, Article 8**, Information to and training of employees, and elsewhere. If you have not received any training, contact your employer, who is required to provide it.



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