THE ISOCYANATE HAZARD IN THE SPRAYING OF TWO-PACK PAINTS

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ABSTRACT

The standard reaction for synthesis of polyurethanes from isocyanates and polyhydroxy compounds is briefly described. Increasingly this is being used in two-pack paints which when mixed and sprayed produce a polyurethane finish on the article to be painted. This exposes the operator to heavy concentrations of isocyanates, and as much of the material is liquid in aerosol form, the vapour pressure of the isocyanate gives no guide to the degree of hazard. It is suggested that the TLV, where one has been established, is not relevant in considering the hazard of sensitisation; this may occur after exposure to concentrations below the TLV.

A number of cases are described, which occurred chiefly in garages and other small establishments, and also the action taken, through the Factory Inspectorate, to require the manufacturers of these paints to issue recommendations for their safe use, including the use of an air-line respirator.

It has been known since the early 1950s that the use of isocyanates, notably toluene di-isocyanate (TDI), in industry for the manufacture of polyurethane foam entailed a risk of respiratory sensitisation, causing occupational asthma.

The reaction depends on the presence of two highly reactive NCO groups in the molecule. These will react with hydroxyl groups to form a polyurethane polymer:

In the foam industry, TDI is the isocyanate of choice for the making of flexible foams, while for rigid foams less volatile compounds such as MDI (4:4 di-isocyanato-diphenyl-methane) are used. It is generally believed that MDI and

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other high isocyanates present a less severe hazard in foam manufacture because of their lower vapour pressure. The present accepted threshold limit value for TDI is 0.02 parts per million in air, or one part in 50 million; but there is evidence that sensitisation can occur after exposure to lower concentrations than this. TLVs do not represent a law of nature, but rather a level which it is practicable to attain and which current experience has suggested is above that likely to cause sensitisation. They frequently have to be amended in the light of further experience. Moreover, even in working areas where monitoring indicates that the TLV has not been exceeded, concentrations may for short periods rise above it as a result of spillage and similar accidents, and cause sensitisation.

TWO-PACK POLYURETHANE PAINTS

In recent years the growing use in spray-guns of two-pack polyurethane paints, in which an "activator" or "hardener" containing an isocyanate is added immediately before spraying, has exposed users in many small industries where a polyurethane finish on the sprayed article is required to a hazard for which they were unprepared and against which employers and employees were inadequately warned.

Case 1

My own first encounter with such a case was on 30 August 1974. A sprayer in a firm of motor body repairers used a newly introduced two-pack paint for some months intermittently, with no ill-effects. He then developed tightness of the chest and dyspnoea, which disappeared when he took a few days off, but recurred shortly after his return to work. At the time of my visit, he was again off sick. The sprayer who took his place had similar symptoms in milder form which lasted only a few hours, and had not so far recurred.

The spraying was done in a large, completely enclosed booth with effective downdraught through the floor. The only form of respirator in evidence was a papiermaché one, but it was said that the absent sprayer possessed one of cartridge type.

The paint additive was of French manufacture, and although the container stated that it contained toluene and xylene, there was no mention of isocyanates. Advice issued to users was simply to mix in a well-ventilated place and "avoid inhaling the vapour". Subsequent analysis of the material by the Industrial Hygiene Unit of the Factory Inspectorate showed it to contain isophorone disocyanate (an aliphatic compound).

Since the hazard in paint spraying consists of the presence of the isocyanate in liquid form, the lower vapour pressure of MDI and other higher isocyanates is irrelevant so far as the exposed worker is concerned. Work at the Occupational Hygiene Laboratory established that the reaction with polyols was quite slow, occupying several hours, and that the spray-mist contained pre-polymers, about whose effect nothing was known, with unreacted iso-cyanate adhering. In these circumstances full protection of the sprayer against inhalation was essential.

Case 2

While these investigations were going on, I encountered my second case, on 29 July 1975. I learned from a Careers Officer that a trainee paint sprayer employed in a garage had sought his help in finding another job, on the grounds that the work was "affecting his chest". I visited the garage, and found that not only the trainee but six other employees, including the manager, had had chest tightness after a two-pack paint had been introduced.

In this garage there were no spray booths; spraying was done against an outside wall in which a row of fans was set at a height of about one and a half metres. In the absence of canopy or partitions, spray was dispersed to parts of the shop where workers doing other jobs were employed. The manufacturers supplied full information about this product, which they said consisted of an acrylic resin in xylol and cellulose acetate, with an activator or converter consisting of a polyisocyanate (Desmodur N), the analysis of which by the Industrial Hygiene Unit showed was based on HDI (hexamethylene di-isocyanate). This firm issued a Data Sheet recommending the use of an air line respirator or one with an activated carbon cartridge and saying the product should be sprayed only in a "well-ventilated area". After correspondence with me they amended this to include specific reference to spray booths with frequent air changes.

Case 3

A small firm manufacturing induction heaters using HF radio waves employed a single paint sprayer, who sprayed the finished products according to customers' specifications. This man developed symptoms like hay fever in the summer of 1975, which recurred with increased severity after a period off work. After this he was transferred to a bench fitting job. He was not happy in this, and asked to return to spraying. This time he developed a streaming nose, swelling around the eyes, and tightness of the chest. At this point he left of his own volition. He had previously had 18 years symptom-free experience as a paint-sprayer.

The spray booth was unexceptionable, with effective exhaust ventilation. It had not occurred to the firm to relate the sprayer's symptoms to the use of any particular paint; but inspection of the labels on the cans in the store revealed one reading "Two-Pack Polyurethane Spraying Hardener". The directors then recalled that one customer had specified a finish with this particular paint, and further research showed a correlation between its use and his symptoms. A telephone call to the manufacturers' technical department confirmed that an isocyanate was used. The caution on the label gave an inadequate warning: "Use in a well-ventilated place. Avoid inhalation of spray mist and contact with skin".

The makers appeared to think that as isocyanate concentrations in the mist had been found to be well below the Threshold Limit Value, there was no serious hazard; but for most aliphatic di-isocyanates no TLV has been fixed, and

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it is impossible to say with confidence that sensitisation cannot occur at concentrations lower than the current TLV, when one has been established.

During, 1977, three more cases came to my notice.

Case 4

A paint sprayer had used a two-pack polyurethane paint for two and a half years, and for the preceding 6 years had been a stove enameller. He suffered from nasal polypi and chronic sinusitis. Shortly after using the paints, he began to suffer from frequent headaches and feelings of lethargy. Some weeks before my visit he was absent from work for some weeks with a respiratory illness, of which the principal symptoms were an unproductive cough and tightness of the chest. He resumed work for 3 days and had a recurrence of symptoms, necessitating a further week off work. The spraying was done in an aerospray booth with a dry-back filter. He had been using a cartridge type respirator, but on my advice changed to an air-fed one.

The adjacent mixing room was too small, and very congested. The job was about to be moved to a new building with much more space, incorporating a separate mixing room with exhaust ventilation. The warning on the container was inadequate, despite the agreed code of the Paint Manufacturers' Association. It said simply "Use in a well-ventilated atmosphere and avoid inhalation of the vapour".

Case 5

This was brought to my notice by a consultant physician, who wrote to say he had a patient complaining of cough and wheezing after spraying with the same product as Case 2. This man was self-employed, renting a workshop on an industrial estate. I visited him, and found he had had tightness of the chest and shortness of breath recurring each time he used this paint, and taking longer to pass off each time. His shop had no spray-booth, but simply a large extractor fan in the rear wall. He had an ill-fitting cartridge type respirator. The rent and rates of his premises cost him £ 3000 per year, and he could not afford to install a booth. He had no access to a compressed air source, and said he would find a simple airline respirator with its distal end outside impossibly cumbersome. In these circumstances it was not possible to do more than ensure that he fully understood the risk and would take the best steps he could to protect himself.

I asked to see the advice supplied by the manufacturers with the paint. There was no sign of the recommendations agreed by the Paint Makers' Association.

Case 6

This case differed from those preceding in being one of skin sensitisation. A man with 30 years service in the paint shop of a firm of motor factors repairing commercial vehicles developed irritation and swelling of the eyelids, orbits and hands, necessitating a month off work. On his return, I was asked to see him. Within three days of his return, his skin trouble recurred, and he left to take up another job.

This man had been using a large number of paints, among which was a two-pack polyurethane one. It was not possible to establish with certainty the particular material to which he was sensitised; but the firm was quite unaware of any respiratory hazard from the two-pack paints, and there was no evidence in their stores or office that any warning leaflet had been supplied with them.

RECOMMENDED WARNING TO USERS OF TWO-PACK POLYURETHANE HARDENERS

During 1976 meetings were held between the Factory Inspectorate, the Paint Makers' Association of Great Britain, the Vehicle Builders' and Repairers Association and the Motor Insurance Repairs Centre in an effort to ensure that all users of these paints, especially in small garages and motor body repair shops, were fully informed about the hazard and the necessary precautions. Agreement was reached that all manufacturers would issue with the paints warnings and advice about safe use, and these were:

- Label to say hardener contains an isocyanate which can affect respiratory system.
- Use only in well-vented enclosure.
- All operators in spray area should wear air-line breathing apparatus during spraying.
- For short exposure under 15 minutes Respirator BS2091; 1969 with type CC canister may be used.
 - However, it takes time for recommendations of this kind to reach every user.

CONCLUSION

The hazard of isocyanate sensitisation is less serious than many but the social consequences to a man who is forced to change his job are none the less important, and the widest possible dissemination of information about the risks and preventive measures must be ensured. This is a comparatively new field of application for isocyanates, and because the material is in the form of mist rather than vapour, the experience of foam manufacture is not-entirely relevant.

It is to be hoped that the voluntary code of practice now agreed in Great Britain will ensure proper protection for the growing number of users of these useful paints.