IOM ADHESIVES SECTION

ADHESIVES FOR A FRIENDLY ENVIRONMENT

Thursday 9th December

Society of Chemical Industry
Belgrave Square
INSTITUTE OF MATERIALS ADHESIVES SECTION
ADHESIVES FOR A FRIENDLY ENVIRONMENT

Thursday 9th December 1993
Society of Chemical Industry, Belgrave Square, London

PROGRAMME

9.45 Registration

10.15 Environmental Issues and Adhesives; A General Review
S G Abbott, SATRA Footware Technology Centre, Kettering.

10.45 Reduction of Solvents in Adhesives
M Cook, Evode, Stafford.

11.15 Coffee

11.40 Ozone Friendly Solvents for Cleaning
C McKenzie, ICI, Runcorn.

12.10 Adhesives and Wastepaper Cycling
K Cathie, PIRA, Leatherhead

12.40 Lunch

14.00 New Curing Agents and Catalysts for Friendlier Epoxy Adhesive Formulation
N T Hunt and W R Ashcroft, Anchor Chemical (UK) Ltd, Manchester.

14.30 Film Adhesives - A 'Green' Alternative
A Bush and J A Stowell, Ciba Composites, Duxford

15.00 Tea

15.20 Panel Discussion

Institute of Materials, 1 Carlton House Terrace, London SW1Y 5BD
Registered with Charity number 269275
IOM Adhesives Group Committee

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Environmental issues and adhesives: a general review

S G Abbott

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Introduction

In the fields of workplace health and safety and control of environmental pollution, all-embracing legislation and regulation is increasingly replacing industry - or substance - specific measures. Many industrial processes using potentially hazardous substances, such as adhesives, albeit on a small scale, face formal control for the first time. Increasing awareness of environmental issues on a broad front and pressures from the 'green' lobby present further challenges which adhesive manufacturers and users must address. These include recycling of materials, environmental auditing and ecolabelling.

Health and safety in the workplace

Apart from specific hazards such as the flammability of solvents and risk of burns with hot melts, adhesives in general tend to produce potentially harmful vapours and may be harmful to skin and eyes. Depending on the quantities used, mechanical extraction of vapours may be necessary; skin and eye contact must be prevented by gloves and goggles wherever risks of contamination or splashing are possible. It is the responsibility of adhesive suppliers to correctly label their products for transport and use and provide appropriate written health and safety data.

In the UK the COSHH (Control of Substances Hazardous to Health Regulations) 1988 replaced much out of date legislation with a comprehensive approach to the control of exposure to virtually all substances hazardous to health, in all work situations. They apply not only to industry but also to universities and research laboratories. COSHH is mirrored elsewhere and is a model for likely European regulations.

The action required falls into five basic sections:

Assessment of health risks in all work activities; control; monitoring of exposure levels; health surveillance; instruction, training and information. Keeping of regularly updated records, for inspection by an official from the Health & Safety Executive, is a key part of COSHH.

Stocks of adhesives must be stored under suitable conditions and any working container to which bulk stocks are transferred must be labelled with the product name, hazards and warning labels as on the original package. Waste adhesive and empty containers must be disposed of in line with regulations.

Control of environmental pollution

Pollution issues

Concerns relating to pollution include:

- General contamination of the environment - air, soil, water - by toxic or harmful substances.
- Damage to the ozone layer in the upper atmosphere, especially by the chlorofluorocarbons (CFCs) and chlorinated solvents, allowing an increase in harmful UV radiation from the sun.
- The 'greenhouse effect' due to increased atmospheric levels of gases, such as carbon dioxide from combustion of fuels and methane from biological sources, restricting the re-emission of solar radiation and leading to global warming.
- Interactions of gases in the atmosphere leading to 'chemical smogs' and 'acid rain'.
Of these the adhesive constituents such as solvents, reactive monomers, curing agents may contribute to the first, and chlorinated solvents to the second. In some instances reactive species become locked into the cured adhesive and escape to the environment is minimal.

Solvents in adhesives and in cleaners and primers used for surface treatment are a contributor to ozone formation and 'smog'. The volatile organic compounds (VOCs) participate in complex chemical reactions in which light energy converts oxygen in the air to ozone. Ozone in the upper atmosphere (stratosphere) is beneficial, forming the protecting ozone layer, but nearer the ground (troposphere) it is harmful to biological processes at concentrations as low as 0.1 parts per million. It is a major contributor to the photochemical smog formed when pollution levels, sunlight intensity and geographical conditions are favourable which aggravates respiratory complaints and assists in acid damage to vegetation. The widely dispersed sources of VOCs means that control measures aim to embrace even small scale users. A United Nations protocol aims for a 30% reduction in VOC emissions by 1999 and a draft European Community Directive aims to control many solvent using processes.

**Environmental legislation**

In the UK the Environmental Protection Act 1990 replaces much old legislation with one all-embracing act. Part I is concerned with pollution control and has enabled the issue of The Environmental Protection (Prescribed Processes and Substances) Regulations 1991. These define various prescribed processes as either Part A, for central control by Her Majesty's Inspectorate of Pollution, or Part B for local authority air pollution control.

Operators of prescribed processes must apply for authorisation on a set timescale. Once the application is determined the authorisation as granted lays down conditions, and these will include emission levels for pollutants and the date by which these must be achieved.

Sections of the EPR relevant to adhesives manufacturers and users cover di-isocyanate processes; coating process and printing; manufacture of dyestuffs, printing ink and coating materials; processes involving rubber.

The EPA is a response to EC Directives and similar legislation is expected in other European states in due course. Germany has the somewhat less stringent TA Luft regulations for controlling air pollution, and the USA the VOC (volatile organic compound) regulations.

**Controlling VOC emissions**

The biggest technical challenge facing adhesives users is in meeting the standards for emission of VOCs, whether these are released from the adhesive itself or from a cleaning or pretreatment process. National strategies rely variously on restrictions on formulation to limit VOC contents; total mass of VOCs emitted; concentration of VOCs in emissions; or some combination of these.

In the UK processes using more than 5 tonnes per year of solvents at a location must reduce VOC emissions to 50mg (as carbon) per cubic metre of vented air by April 1996. This requirement is encouraging the substitution of solvent preparations by water-borne or hot melt systems. However, these may have drawbacks such as specialist application equipment, extended drying times or closely controlled working times, limited tack and variable bonding performance. For demanding applications, such as shoe sole bonding, low-solvent adhesives are not yet sufficiently versatile to fully displace solvent-borne adhesives; moreover, solvent-based cleaners and pretreatments may continue to be necessary. Some adhesive using industries are likely, therefore, to require solvent arrestment measures. Adsorption on carbon beds is feasible but mainly suited to processes using a single solvent of low water solubility which can be recovered by steam stripping. More generally, mixed solvents will be best handled by thermal or catalytic incineration.

**Waste management**

Disposal of factory waste is being increasingly controlled. In the UK a new 'duty of care' applies from 1st April 1992 to all who produce or handle waste; waste producers must properly describe their waste and transfer it only to an authorised person. Certain difficult or dangerous wastes
are classified as 'special waste' and are subject to additional regulations and higher disposal costs. Adhesive users should aim to restrict the amount of waste generated, for example by ensuring that containers are as completely emptied as possible in use. Residual contents can be minimised by evaporation or incineration before disposal.

Post-consumer waste is a growing concern especially in relation to short life products such as packaging; however, any adhesive used forms a low proportion of the total volume and is unlikely to attract specific attention providing it is fully cured and non-hazardous.

**Other environmental issues**

**Recycling**

Recycling of materials after a service life in a consumer product has a high public profile. Attempts to recover adhesives are unlikely, but tailoring of adhesives to ease recycling of bonded materials is receiving increasing attention. This is especially relevant to paper and board packaging, where recycling requires mechanical or chemical methods to remove adhesive particles. More generally, design of assemblies for ease of dismantling and separation of dissimilar materials requires joints which can be readily disbonded without compromising service performance!

**Environmental auditing and ecolabelling**

An environmental audit of a manufacturing process helps to demonstrate to customers and the community that a company is complying with legislation and acting responsibly in environmental terms. Environmental auditing normally addresses all stages of the manufacturing process, including raw materials and energy usage, materials processing, emission of pollutants and generation of waste. Adhesives are most likely to receive attention if they generate polluting emissions, such as solvents.

British Standard BS 7750 : Environmental Management Systems provides a means of establishing a documented system for delivering an environmental policy. The EC Eco Management and Audit Regulation requires companies to establish such a policy and produce a validated public statement of environmental performance; participation is voluntary.

The growing demand for green products has led to the appearance of 'environmentally-friendly' labels but these have usually been unofficial or based on questionable claims. The EC ecolabelling scheme, with its 'flower' logo, aims to provide an official guide to consumers on goods that cause the least damage to the environment. Criteria for an award of an ecolabel are based on a 'cradle to the grave' life cycle analysis, including water use, water/soil/air pollution, noise and consumption of energy and resources.

The products for which ecolabels are in prospect are those with the greatest environmental impact, such as paper and detergents. Products using adhesives in their assembly, such as washing machines and footwear, are included. In general, materials forming less than 5 per cent of a product are excluded, subject to weighting for environmental impact, so adhesives may escape attention unless they cause polluting emissions.

**Energy**

All forms of energy have an environmental impact, in particular the contribution to the 'greenhouse effect' from combustion of fossil fuels. Adhesive bonding is a relatively low energy user and may compare favourably with other assembly processes such as welding, although the energy used to produce the adhesive itself must be taken into account.

**Renewable resources**

Some consumers are keen to use products based on natural, renewable resources, although green materials are not without environmental impact. This may favour adhesives based on natural substances, either for assembling a green product or for the retail adhesive market. Adhesives produced by biotechnology are a development of natural adhesives which is the subject of current research.
REDUCTION OF SOLVENTS IN ADHESIVES

DR MIKE COOK

EVODE LIMITED

Solvent based adhesives are currently used in a wide variety of industrial and DIY bonding applications. They are used in most industries including packaging, construction, footwear, furniture and automotive for bonding a wide variety of substrates such as wood, fabrics, foams, metals, rubbers and plastics.

A very extensive range of raw materials is available for use in the formulation of solvent based adhesives. These include various polymers, tackifying resins, solvents, fillers and miscellaneous additives. As a result it is now possible to formulate solvent based systems with a very wide range of properties to meet the requirements of most customers, even for the most demanding applications.

We therefore need to ask the questions :-

Why do we need to reduce solvents in adhesives?

Although there are a number of answers to this question the two over-riding ones are:-

2. Environmental legislation.

Most solvents used in the formulation of adhesives are affected, in one way or another, by this legislation. Although it is possible to manufacture and use solvent based adhesives and still meet the current and proposed legislation, the procedures required to do so, for example solvent recovery and solvent incineration, are likely to be very expensive and prohibitive to a large number of end users and even some adhesive manufacturers.

There are a number of so-called "safe and environmentally friendly" solvents commercially available but, at the present time, these appear to have limited application in the field of adhesives. One area where they do show considerable promise is in the formulation of PVC pipe cements. In fact Evode has just launched a patented system called Pevicol which is based on such a solvent, namely, N-methyl-2-pyrrolidone. The performance of this system is comparable to that of conventional pipe cements. From past experience, however, a solvent which is classed as safe and environmentally friendly today is likely to be considered unsafe and/or environmentally unfriendly tomorrow. As a general approach, therefore, the use of such solvents would only appear to be a short term answer to the problem.

Another approach could be the use of high solids adhesives but once again this is only seen as a short term answer.
The long term answer to the problem of solvent based adhesives is to find suitable alternative systems. There are three basic alternatives, namely:

1. Water based adhesives.
2. Hot Melt adhesives.
3. Liquid, reactive adhesives.

All of these systems have been available for a long time and over the years they have all successfully replaced solvent based adhesives in a number of industrial and DIY applications. However, there is still a very long way to go especially in the area of high performance systems. Not one of the above systems is the ideal alternative in all applications. Each has its own advantages and disadvantages and the one chosen will depend upon a number of factors, including: substrates being bonded; application conditions; cost and performance requirements of the bonded assembly. It is almost certain that these alternative systems will eventually replace solvent based adhesives in the majority of industrial and DIY applications but the time-scale involved is difficult to predict since it will depend upon two main factors:

1. Legislation.
2. Technology Development.

Let us consider one of these alternative systems, namely water based adhesives, in more detail. One convenient way of classifying water based adhesives is by the method of bond formulation and using this procedure we obtain four basic classes:

1. Contact adhesives.
2. Heat activatable adhesives.
3. Wet bonding adhesives.
4. Pressure sensitive adhesives.

We have the same four basic classes with solvent based adhesives.

Let us now consider contact adhesives and see how the water based systems compare with the solvent based systems. This comparison will be carried out in a very general way.

The majority of solvent based contact adhesives are based on polychloroprene polymers. A large number of such polymers are commercially available from a number of suppliers. The components of a typical contact adhesives are, polychloroprene polymer(s), resin(s), solvent(s), metal oxides and antioxidant.
By careful choice of these raw materials, adhesives with a very wide range of properties can be produced. Such adhesives are used in the DIY market and in a wide range of industrial applications, mainly in the furniture, automotive, construction and footwear industries. They are characterised by high initial and final bond strength, good adhesion to a wide range of substrates, good heat resistance, bond flexibility, ease of application and a wide range of formulations to meet specific requirements.

The obvious starting point for a water based contact adhesive is a polychloroprene dispersion. Such dispersions have been available for a long time and a large number are now commercially available. As with the solvent based systems a resin is required to tackify the polychloroprene dispersion. Originally resin solutions containing a solvent such as toluene were used. There have been major resin technology advances over recent years and as a result a large number of stable, solvent free resin dispersions are now readily available. For obvious reasons these resin dispersions are now preferred to the resin solutions. In addition, various additives are used in order to impart specific properties.

It is now possible to produce a solvent free, general purpose, polychloroprene dispersion based contact adhesive with good overall properties. The results obtained with currently available products, however, are still inferior to those achievable with solvent based systems, particularly with regard to contactibility, greenstrength and adhesion versatility. Despite this, such systems have replaced, and are still replacing, solvent based products in a number of DIY and industrial applications.

If water based contact adhesives are to make serious inroads into the solvent based market then major technology advances are required. This is beginning to happen with the development of new polymer dispersions, eg polyurethanes and acrylics which can be used as alternatives to, or as blends with, polychloroprene dispersions. Work carried out at Evode over the past 12 months has shown that it is possible, in certain instances, to produce a contact adhesive using a blend of two polymer dispersions which exhibits the good performance characteristics of the individual dispersions, eg with a polychloroprene/polyurethane blend we have developed a product with the good contactibility properties of the polychloroprene and the good adhesion properties of the polyurethane. This work is still in its infancy but the technique of polymer blends appears to offer considerable scope for future development.

In summary we can say that current and proposed health and safety and environmental legislation is putting a considerable amount of pressure on both manufacturers and end users of solvent based adhesives. The long term answer to this problem is to develop suitable alternative systems such as hot melt, water based and liquid reactive adhesives.
OZONE FRIENDLY SOLVENTS FOR CLEANING

C S McKenzie
ICI Cleaning Technology Business

SUMMARY

The Montreal Protocol is an international agreement, signed by over 100 countries, designed to phase out man-made ozone depleting substances within a defined timescale. Two very versatile solvents, 1,1,1-trichloroethane and CFC 113, are affected. The original protocol was signed in September 1987, but since then several subsequent revisions to it have brought forward the phase-out dates. Many regions around the world have their own tougher regulations, for instance the European Community has its' regulation EC 3952/92. This states that ALL EC countries must meet the following phase-out schedule:

1,1,1-trichloroethane - 1/1/94  Production cut to 50% of 1989 levels
- 1/1/96  Phase-out

CFC 113
- 1/1/94  Production cut to 15% of 1986 levels
- 1/1/95  Phase-out

The phase-out of these two widely used solvents means that end-users will need to re-evaluate their processes and operations with a view to switching to an alternative, non-regulated substance.

Fortunately, there are alternative chlorinated solvents currently available, which do not deplete ozone and are therefore not regulated under the terms of the Montreal Protocol. Examples of these chlorinated solvents are trichloroethylene, perchloroethylene and methylene chloride.

1 WHY DO WE CLEAN?

The need for cleaning arises because of contamination with soils during the handling or production of articles which have to be further treated in downstream activities. Examples of soils can be fingerprints, cutting/pressing oils, dust or even a protective coating. If an article is to be coated or have an adhesive applied to it, (eg painted or glued) then removal of the contamination is an essential part of the process.
2 HOW IS THIS ACHIEVED?

There are various methods of cleaning. The choice is very much dependant on the type of article to be cleaned, throughput, standard of cleanliness required and the type of contaminant. Common methods of solvent cleaning are “cold cleaning” and “hot vapour cleaning”. Cold cleaning can be further sub-divided into the four main categories:

Dipping - usually performed in a purpose built tank.

Wiping - solvent is applied using a cloth and it is the mechanical action of the wiping together with the solvent which removes the soils.

Brushing - generally used to dislodge particles which would not normally be removed by either dipping or wiping.

Spraying - most effective with large droplets of solvent using an airless spray and is particularly effective where access with brush or cloth is restricted.

Finally, vapour cleaning. This will be the most economical method of cleaning in terms of solvent usage since by its very nature it has to take place in purpose built equipment, which although traditionally has been open-topped is now becoming more and more enclosed. Hot cleaning plants can incorporate many features eg:

Vapour Only - where the action of hot solvent vapour condensing on a cold article “washes” off grease and other contaminants.

Boiling Liquid & Vapour - where the vapour cleaning is supplemented by the addition of a boiling liquid stage.

Vapour & Spray - distilled liquid is sprayed (via a pump) onto the article to assist the vapour.

Ultrasonics - the use of cold ultrasonics can be added to all of the above processes to help cleaning.

Vapour cleaning can be operated as either batch or continuous process.

3 CRITERIA FOR CHOOSING A SOLVENT

The criteria for choosing a solvent can be briefly summarised into the following major categories:

a) Safety - Toxicology of the product.

   Flammability.

   Stability.


   Greenhouse Warming Potential.

   Photochemical Ozone Creation Potential.
c) **Effectiveness**
- Surfaces need to be grease free to allow good adhesion.

d) **Costs and availability**
- Capital outlay
- Installation costs
- Energy consumption
- Disposal of waste streams

### 4 NON-MONTREAL PROTOCOL CONTROLLED CLEANING SOLVENTS

The following chlorinated solvents do not deplete ozone, are not greenhouse gases and have very low POCP values:

a) **Trichloroethylene**

b) **Perchloroethylene**

c) **Methylene chloride**

They are also excellent solvents for a wide range of contaminants and can readily replace 1,1,1-trichloroethane and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113) in vapour cleaning applications.

The chlorinated alternatives, listed above, can also be used for cold cleaning operations provided that there is sufficient ventilation to ensure worker exposure is maintained below the National Occupational Exposure Limits (OEL's).

However, the favoured alternative in cold cleaning operations is refined hydrocarbons, which also do not deplete ozone. These specialist hydrocarbon formulations are particularly suited to cold cleaning due to their ability to dissolve oil and grease.

Finally, aqueous or semi-aqueous cleaning. These processes utilise the action of detergents and other chemicals to help solubilise the oils and greases that may be present, before rinsing off with clean water. An additional drying stage is usually required in these processes.

For further information please contact:

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ADHESIVES AND WASTEPAPER RECYCLING

K Cathie
PIRA, Leatherhead

Abstract

This paper will cover four areas:

* the importance of wastepaper as a raw material for paper and board manufacture in the UK
* problems that adhesives cause in paper and board recycling
* how recycling mills tackle the problem of adhesives
* how can adhesives be made so that they are more 'mill friendly'.

The importance of wastepaper as a raw material for paper and board manufacture

Wastepaper is a very important raw material to the UK paper and board industry. In 1991, approximately 4.9 million tonnes of paper and board were produced using 2.9 million tonnes of wastepaper. This means that over 60% of the fibrous material used for paper and board manufacture was derived from wastepaper.

Traditionally most wastepaper in the UK has been utilised in packaging and board products where the aesthetic value was not of prime importance. Less wastepaper has been used in higher standard products such as printing and writings and tissue. However, this situation is set to change.

Problems that adhesives cause in wastepaper recycling

There is no doubt that the greatest problems experienced by wastepaper-using mills are caused by adhesives. Once in the recycling system these adhesives form tacky particles which are generically known as stickies. Stickies are usually chemically complex comprising of papermaking chemicals and coatings as well as adhesives.

Stickies can affect the whole of the recycling operation from the processing of the wastepaper, to the papermaking stage, to the conversion of the paper and board into
a product.

Estimated costs borne by mills due to stickies in relation to one hours papermachine downtime alone can be high as £10,000 for a large newsprint mill producing 200,000 tonnes per year.

How recycling mills tackle the problem of stickies
Due to the enormity of the problems caused by stickies, dedicated equipment is installed in all wastepaper-using mills to try to counteract their effect. Wastepaper treatment is a multistage process. Each stage being designed to remove or mask contaminants, which are primarily stickies, or ensure that they remain in a form so that they can be removed or controlled. Essential stages include:

* pulping
* screening
* cleaning
* dispersion.

As well as mechanical treatments to deal with stickies many mills also use chemical control methods. The three most popular are:

* passivation
* dispersion
* ionic sprays.

How can adhesives be made so that they are more ‘mill friendly’?
This is probably one of the most confusing issues facing adhesive manufacturers and their suppliers today as unfortunately there is no totally clear cut route to take. However, generally adhesives will be more ‘mill friendly’ if they have one of the following characteristics:

* produce hard, large non-tacky lumps on pulping
* have a density significantly higher or lower than that of the pulp suspension (1g/cm³)
* be water dispersible.
The characteristics that can be adopted by adhesives will obviously depend on adhesive type, application etc. In addition the response of the adhesive at the wastepaper processing stage will depend on the mills operating conditions.

Small, perhaps seemingly simple changes to adhesives can help the wastepaper user.
New Curing Agents and Catalysts for Friendlier Epoxy Adhesive Formulations.

N.T. Hunt and W.R. Ashcroft
Anchor Chemical (U.K.) Ltd, Manchester, England

Abstract
This paper highlights how environmental issues and increasing legislation in the epoxy market has seen the introduction of novel, non-toxic hardeners in adhesives applications. Epoxy resins can be converted to infusible thermoset materials by cross linking agents i.e. polyfunctional amines which have a wide use in many industrial applications including the adhesive sector. There are several factors important to the durability of an adhesive bond including the joint design, adherend preparation and service temperature which is in part related to the glass transition temperature of the polymer system.

Modification or replacement of curing agents to safer handling, environmentally friendly offsets is a considerable concern of all raw material suppliers and formulators. New low viscosity modified polyamides are expected to replace standard polyamides in many adhesive formulations as a result of their improved handling and performance characteristics. The aromatic amines previously labelled 'Harmful' under new legislation now carry the R45, 'may cause cancer', risk phrase. Polycycloaliphatic polyamines have shown comparable performance to the plasticised, accelerated aromatic systems which may offer themselves to high performance applications. In heat cure systems, lower oven temperatures and shorter post bake times, to decrease the energy consumption, are among the driving forces for product re-formulation. The dicyandiamide co-accelerators Monuron and Diuron (chlorinated aromatic ureas) used typically in the automotive and aerospace industries are also being replaced with non-toxic performance offsets which offer the added advantage of faster green, handling strength.
New Curing Agents and Catalysts for Friendlier Epoxy Adhesive Formulations

N.T. Hunt and W.R. Ashcroft
Anchor Chemical (U.K.) Ltd, Manchester, England

1. Introduction.

To convert epoxy resins to hard, infusible thermosets it is necessary to use crosslinking agents. The hardeners may promote the crosslinking by either homopolymerisation or with a multifunctional curing agent, by polyaddition. The temperature range over which an adhesive must retain its integrity is, after the correct joint design, the most important characteristic. Synthetic polymers come with a well defined glass transition temperature (Tg) which is primarily influenced by two factors: the molecular structure of the polymer and the curing temperature. The definition of glass transition temperature can be related to polymer behaviour i.e. a rigid, glassy material below Tg which then passes through a tough and rubbery phase (viscoelastic area) as temperature increases. The change of properties is reversible for thermoplastics, but irreversible for thermosets (epoxies). Structural adhesives therefore are formulated such that the exposure temperatures is not much above the Tg of the resin / curing agent system. If the adhesive is continuously exposed to high temperatures, a Tg above these temperatures is advisable to prevent long term creep in bonded joints. Table 1 indicates the formulating versatility of epoxy thermoset adhesives: the one pack heat cure systems show higher Tgs than ambient cure two pack systems which is due in part to the effect of elevated cure temperatures which promote higher crosslink densities and in part to the fact that latent hardeners generally do not contain plasticisers and are 100% reactive systems.

Table 1 Glass Transition Temperatures (Tg) and Service Ranges for Epoxy Adhesives.

<table>
<thead>
<tr>
<th>Adhesive Type</th>
<th>Curing Agent</th>
<th>Tg (°C)</th>
<th>Service Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TWO PACK</td>
<td>Polyamide</td>
<td>45</td>
<td>-50 to +30</td>
</tr>
<tr>
<td></td>
<td>Formulated aliphatic polyamine</td>
<td>95</td>
<td>-30 to +80</td>
</tr>
<tr>
<td></td>
<td>Formulated aromatic polyamine</td>
<td>60</td>
<td>-50 to +45</td>
</tr>
<tr>
<td></td>
<td>Mercaptan</td>
<td>50</td>
<td>-100 to +40</td>
</tr>
<tr>
<td>ONE PACK</td>
<td>Aromatic Polyamine</td>
<td>165</td>
<td>-30 to +150</td>
</tr>
<tr>
<td></td>
<td>Dicyandiamide / Urea</td>
<td>130</td>
<td>-30 to +110</td>
</tr>
<tr>
<td></td>
<td>Monoanhydride / tertiary amine</td>
<td>140</td>
<td>-30 to +130</td>
</tr>
<tr>
<td></td>
<td>Dianhydride</td>
<td>290</td>
<td>-30 to +270</td>
</tr>
</tbody>
</table>
2. Issues with Existing Curing Agent/ Catalyst Technologies.

Table 2 Current Environmental Issues with Epoxy Curing Agents.

<table>
<thead>
<tr>
<th>Adhesive Type</th>
<th>Curing Agent</th>
<th>Improvement Opportunities</th>
</tr>
</thead>
<tbody>
<tr>
<td>TWO PACK</td>
<td>Polyamide</td>
<td>Viscosity / VOC reduction</td>
</tr>
<tr>
<td></td>
<td>Formulated aliphatic polyamine</td>
<td>Toxic Accelerators Elimination</td>
</tr>
<tr>
<td></td>
<td>Formulated aromatic polyamine</td>
<td>Toxicity Base Amine Elimination</td>
</tr>
<tr>
<td></td>
<td>Mercaptans</td>
<td>Odour Reduction</td>
</tr>
<tr>
<td>ONE PACK</td>
<td>Aromatic polyamine</td>
<td>Toxic Base Amine Elimination</td>
</tr>
<tr>
<td></td>
<td>Dicyandiamide / Urea</td>
<td>Toxic Urea Catalyst Elimination</td>
</tr>
</tbody>
</table>

Current market requirements in epoxy adhesive formulation are leading to more environmentally conscious products. Legislation on VOC levels has seen the introduction of high solid and water borne adhesives in many bonding applications. Most polyamides are relatively viscous and require solvents to optimise wetting and adhesion. Phenolic accelerators used to improve the compatibility and low temperature cure characteristics of aliphatic polyamines are under increasing pressure to be eliminated. Aromatic amines used in high performance areas were previously labelled 'Harmful' and now carry the R45 risk phrase, 'may cause cancer'. The thiol or mercaptan group (-SH) reacts with epoxy resin rapidly in an addition reaction usually in the presence of tertiary amines to initiate mercaptide ions. The moisture resistances of the cured systems are low however, due to the beta-hydroxy functionality, and this with the disagreeable odour and skin sensitisation tendency has limited their widespread usage. In one pack heat cure adhesives the need for lower cure temperatures and faster cure cycles is a major driving force for product re-formulation and the standard urea accelerators derived from chlorinated aromatic amines are toxic.

3. New Polyamide Hardeners.

Aliphatic amines such as polyethyleneamines can form condensation reactions with carboxylic acids to form amides which can overcome the volatility, high vapour pressure and critical loading associated with the base amines. Commercially available polyamides based on fatty acid, dimer acid and ethylenamines vary greatly in molecular weight, physical form and reactivity but all have low volatility and hence low irritation potential. The mixing ratios with epoxy resins are generally non-critical and the cured properties can be modified from tough at below stoichiometry to soft and flexible at higher loadings. The hydrophobic fatty acid polymer provides excellent corrosion resistance by its water repelling nature which avails these systems to underwater, high moisture tolerance adhesives. They generally show good adhesion to a wide range of substrates due to the residual secondary amine functionality on the polyamide backbone which provides keying in sites or hydrogen bonding. Polyamides are, however, rather slow to cure especially at
lower temperatures due to their slow diffusion and the 'solvent like' effect of the fatty acid polymer backbone although the reactivity can be improved by addition of tertiary amine accelerators. The relative low crosslink density produces an open matrix which leads to poor solvent resistance.

A new generation of polyamides are now available which offer improved handling and physical performance over the current industry standards. Table 3 compares some standard parameters; the modified material has lower viscosity, resulting in improved substrate wetting and adhesion as highlighted in the improved low temperature bonding to damp concrete. The viscosity facilitates the use of this material in high solid systems with minimum inclusion of solvent in line with VOC legislation. The modified polyamide shows improved low temperature cure as a dual result of the low viscosity and also the unhindered polyfunctionality of the base amine used in the modification design.

**Table 3 Handling Properties of Standard and Low Viscosity Polyamides.**

<table>
<thead>
<tr>
<th></th>
<th>Std. Polyamide</th>
<th>Low Viscosity Polyamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading (phr)</td>
<td>50-60</td>
<td>50-60</td>
</tr>
<tr>
<td>Viscosity @ 25 °C (mPas)</td>
<td>8000</td>
<td>3000</td>
</tr>
<tr>
<td>Thin film set @ 25 °C (hrs)</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Pot Life @ 25 °C (mins)</td>
<td>200</td>
<td>65</td>
</tr>
<tr>
<td>Labelling Status</td>
<td>Non Corrosive</td>
<td>Non Corrosive</td>
</tr>
<tr>
<td>Adhesion to Damp Concrete</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Pull Off N/mm² @ 25 °C</td>
<td>1.45*</td>
<td>2.07 #</td>
</tr>
<tr>
<td>@ 5 °C</td>
<td>0.41*</td>
<td>1.72 #</td>
</tr>
<tr>
<td>Shore D Hardness</td>
<td>75</td>
<td>80</td>
</tr>
<tr>
<td>Tensile Strength  N/mm²</td>
<td>39.3</td>
<td>58.6</td>
</tr>
<tr>
<td>Flexural Strength  N/mm²</td>
<td>95.9</td>
<td>112.4</td>
</tr>
<tr>
<td>Compressive Strength  N/mm²</td>
<td>90.3</td>
<td>78.0</td>
</tr>
</tbody>
</table>

Key: * = Cohesive Failure     # = Bond failure in the upper 10% of the concrete specimen.
Curing agents mixed with liquid epoxy resin EEW = 190 at 60 phr and cured 7 days @ 25 °C before testing.

Improvements in the high temperature performance of polyamides for two component adhesive applications can be made by combining standard or high performance polyamides with cycloaliphatic polyamines (Table 4).

Adhesion to fibre reinforced plastic and steel was evaluated under the conditions as outlined in Table 4. Using ASTM D1002, samples were cured at ambient temperature and lap shear evaluated at both ambient and elevated, 93 °C.
Table 4 Bond Strength of Ambient Cured Modified Polyamide Adhesives.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>FRP / FRP</th>
<th>Steel / Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Preparation</td>
<td>Dry rag wipe</td>
<td>Acetone wipe</td>
</tr>
<tr>
<td>Cure Schedule</td>
<td>24 hrs. @ ambient</td>
<td>24 hrs. @ ambient</td>
</tr>
<tr>
<td>Lap Shear Strength at 25 °C</td>
<td>Std Polyamide 3.0</td>
<td>Modified 3.2</td>
</tr>
<tr>
<td></td>
<td>Modified 3.2</td>
<td>Std Polyamide 10.5</td>
</tr>
<tr>
<td></td>
<td>Modified 8.3</td>
<td>Modified 8.3</td>
</tr>
<tr>
<td>Lap Shear Strength at 93 °C</td>
<td>Std Polyamide 1.45</td>
<td>Modified 2.2</td>
</tr>
<tr>
<td></td>
<td>Modified 3.9</td>
<td>Modified 5.9</td>
</tr>
</tbody>
</table>

4. Aromatic Amine Replacement.

Aromatic polyamines are formulated in both 2 pack and 1 pack, heat cure, adhesives. Plasticised versions are used in laminating, underwater and chemically resistant adhesives whilst the un-plasticised variants are used predominantly in hot melt and high service temperature, high performance adhesives. Cycloaliphatic and polycycloaliphatic polyamines are finding increasing use as non-toxic replacements in many of these application areas.

Table 5 Aromatic Amine Replacement Application Areas Summary.

<table>
<thead>
<tr>
<th>Application Area</th>
<th>Old Technology</th>
<th>New Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Underwater Adhesives</td>
<td>Aromatic amines with coal tar extenders.</td>
<td>Hydrophobic cycloaliphatics with albino coal tar modifiers.</td>
</tr>
<tr>
<td>High Chemical Resistance</td>
<td>Aromatic amines used with novolac resins.</td>
<td>High cross link density cycloaliphatics.</td>
</tr>
<tr>
<td>Adhesives</td>
<td>Low viscosity aromatics.</td>
<td>High functionality amines.</td>
</tr>
<tr>
<td>Laminating Adhesives</td>
<td>Solid aromatics (DDM).</td>
<td>Long pot life cycloaliphatics.</td>
</tr>
</tbody>
</table>

Polycycloaliphatics are non-toxic and have shown outstanding mechanical properties, high acid and solvent resistance, and similar adhesion compared to standard plasticised aromatics.
Table 6 Properties of Plasticised Aromatic and Non Toxic Performance Offset.

<table>
<thead>
<tr>
<th></th>
<th>Activated Aromatic</th>
<th>Modified Polycycloaliphatic amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading (phr)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Viscosity @ 25 °C (mPas)</td>
<td>&gt;600</td>
<td>450-500</td>
</tr>
<tr>
<td>Pot Life @ 25 °C (mins)</td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>Labelling Status</td>
<td>TOXIC</td>
<td>Irritant</td>
</tr>
<tr>
<td>Adhesion to Concrete</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Pull Off N/mm² @ 25 °C Wet</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Tensile Pull Off N/mm² @ 25 °C Dry</td>
<td>4.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Adhesion to Steel DIN 53151</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Shore D Hardness</td>
<td>73</td>
<td>78</td>
</tr>
<tr>
<td>Tensile Strength N/mm²</td>
<td>35</td>
<td>52.4</td>
</tr>
<tr>
<td>Flexural Strength N/mm²</td>
<td>51</td>
<td>93.8</td>
</tr>
<tr>
<td>Compressive Strength N/mm²</td>
<td>-</td>
<td>71.5</td>
</tr>
</tbody>
</table>

Adhesion to steel DIN 53151 has a rating of 0 = excellent; 5 = very poor

In heat cure, hot setting adhesives for bonding of metals and ceramics solvent free cycloaliphatics such as Bis (p-Aminocyclohexyl) Methane are being substituted for the toxic aromatic amines. The 4,4'- Diamino Diphenyl Methane (DDM) is a solid material and must pre-heated or used with solvent prior to addition with epoxy resin which increases the handling problems. The high reactivity of the low viscosity base cycloaliphatic amine can be adjusted with steric modification i.e.methyl substitution. The high crosslink density of the amine leads to high mechanical properties and excellent chemical resistance with the added advantage of improved fracture resistance important in composite and adhesive applications.


In one pack, heat cure adhesives, market trends driven by environmental issues require non-toxic systems with low activation temperatures, fast cure times and short post bake cycles to decrease the overall energy consumption. Current research programs are concentrating on novel technology to procure these performance goals and obtain higher efficiency, safe co-accelerators. One main area of product re-formulation is replacement of the chlorinated aromatic ureas, Monuron and Diuron, which have toxic labelling status. These are commodity products from the agrochemical industry used as co-accelerators for Dicyandiamide cure. The cure mechanism is believed to involve a deblocking of the urea by dicyandiamide to release dimethylamine which then acts as a standard tertiary amine accelerator. Non-toxic performance offsets have been developed which also offer the advantage of improved green handling strength facilitating early removal of the component.
from the support jig. Differential scanning calorimetry shows a decrease in the activation temperature of the dicyandiamide cure from 186 °C to circa 145 °C with a greater % conversion with the new generation non toxic offsets.

Graphs 1 and 2 Improved Performance of Non Toxic Substituted Ureas.

<table>
<thead>
<tr>
<th>DSC Activation temperature</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Catalyst</td>
<td>2phr Diuron</td>
</tr>
</tbody>
</table>

Measured with Standard Bis A resin / Micronised Dicyandiamide (average particle size 10µ) ratio 100 : 5 wt.%
STRUCTURAL FILM ADHESIVES – A GREEN ALTERNATIVE?

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Introduction
As each very broad class of adhesives will have its own set of arguments as to which format offers the "safest" approach, for the purposes of this presentation, only the field of Structural Adhesives will be considered.

Definitions
There is no succinct definition of a structural adhesive but, in essence, it is an adhesive based on monomer compositions which polymerise to give high modulus, high strength bonds between relatively rigid adherends [substrates] so that a load-bearing joint is constructed.

Although under certain circumstances unreactive [eg thermoplastic] adhesives can, and must, be considered, it is generally accepted that such adhesives will be reactive in nature. A reactive adhesive can be defined as:

A multi-component system which, after application, changes its physical form from essentially/potentially liquidous to infusible solid by chemical reaction [polymerisation and/or cross-linking].

Chemical Classes of Reactive and Structural Adhesives
As has been indicated, a structural adhesive, generally, has to react to build up its final, infusible, cross-linked network; a thermoplastic adhesive, though, which has been melted and allowed to wet the substrate, uses its naturally high molecular weight and very high T, to form structural bonds, on solidification. Typical of these adhesives are those based on PES, PEK, PEEK, PEI, PAPl, etc.

The chemistries associated with the reactive adhesives are:

- Amino-Formaldehyde
- Polyurethane
- Silicone
- Cyanoacrylate
- Anaerobics
- Phenol-Formaldehyde
- Second-Generation Acrylics
- Epoxy
- Polyimide/Bismaleimide

As far as "Green"/Safety matters are concerned, it is how these chemistries are physically handled, both to manufacture and to use the adhesive, which is important.

Generic Types of Structural Adhesive
The above chemistries can be used in several broadly-based compositions to produce structural adhesives and it is this format, rather than the basic chemistry of the adhesive as such, which will, more often than not, determine its effect on the operator [manufacturer and end-user] and the environment.

Thus, most of the above chemistries can be utilised in most of the following formats:

- Solution Adhesive - Solvent Based
- Solution Adhesive - Water Based
- Paste Adhesive - 100% solids
To draw any conclusions as to the overall efficacy of any format, it is necessary to review the pros and cons of each as a separate entity.

However, before doing that, it is important to note that there is one process associated with the use of structural adhesives on metallic adherends which is totally independent of chemical class of adhesive. This is the pretreatment which the metallic substrate requires prior to bonding. The chemistries of these pretreatments tend to be somewhat toxic and corrosive and require specific extract systems, etc to protect the operator and the environment. Work is addressing this problem with the current approach being to try to reduce [it is very difficult to eliminate] the hazards associated with these materials - for example the use of phosphoric acid anodizing of aluminium rather than anodizing in chromic acid.

**Solution Adhesives - Solvent Based**

These adhesives are generally fairly easy to manufacture hence consuming relatively low amounts of energy; even stoving the applied adhesive to remove solvent prior to bonding can generally be accomplished at temperatures between 22 and 80°C. However, such adhesives often require the use of complex blends of solvents which can be both toxic and highly flammable. Typical of the materials which have to be used [to aid solution and stability as well as controlling evaporation rates, etc] are:

- Ketones [acetone, MEK]
- Substituted Glycols [methoxy ethanol, etc]
- Chlorinated Hydrocarbons [methylene chloride, Genclone, etc]
- N-Methyl Pyrrolidone
- Dimethyl Sulphoxide

By the very nature of these adhesives, the possibility of operator contact is high and, as the solvent has to be removed prior to bonding, the potential for damage to the environment is significant. Good operator protection, high quality [flame-proof] extraction and possibly the addition of solvent scrubbers would be required.

**Solution Adhesives - Water Based**

The hazards of using organic solvents are immediately removed with the potential harm to the environment significantly reduced. However as water-based solutions/dispersions are being used the potential for harm to the eco-structure, following any spillage, is significantly increased.

Operator contact still remains a distinct probability but the severity of any such contact is reduced by the use of water; although it must be remembered that precautions might well have to be taken against contact with toxic/acidic stabilisers, anti-fungicides, etc.

The preparation of aqueous solutions/dispersions, of the typical materials used in structural adhesive formulations, can be difficult and hence energy consumption is likely to be higher, especially when the greater difficulty in removing the "solvent" prior to bonding, is considered.

In summary, a safer, if somewhat more energy-consuming, approach to solution adhesives mainly limited by the restrictions on the range of materials suitable as formulating ingredients.

**Paste Adhesives**

Such systems are relatively easy to produce consuming comparably low amounts of energy; such energy saving can be augmented when their potential for
ambient [or very low temperature: eg 40 - 60°C] cure is taken into account.
The use of formulated systems, based on 100% solids, means that there are no
hazards associated with the presence of solvents.

However, as many of the prime ingredients can be skin sensitizers, the high
probability of operator contact, in part due to the tendency to apply an
excess of adhesive into the joint, can lead to a potential hazard. Good
housekeeping, the correct protective clothing and the recently introduced use
of automatic metering and dispensing equipment is minimising this risk.

In summary, a relatively safe and versatile format with significantly high
possibility of skin contact the major drawback.

**Film Adhesives - Cast from Solvent- or Water-Based Solutions**

The comments made on the solvent- and water-based solution adhesives apply
again here; most of the hazards only seen by the manufacturer, not the end­
user. However, once an adhesive film is produced many of the advantages, which
are enumerated later, will apply to these systems.

However, as such systems have been produced by casting continuous films of
formulated matrix from "solution", any retained "solvent" could lead to a
problem further down the line.

Moreover, in the case of the organic solvent-cast films, a suitable scrubbing
device will have to incorporated in-line, to prevent significant vapour
emissions to atmosphere; this will obviously not apply to water-based systems.

Many of these adhesives will require curing at temperatures between 80 and
180°C which will add to the relatively low energy consumptions associated with
their manufacture.

In summary, relatively safe systems which throw most of the onus for
c onsiderable personnel and environmental protection on the manufacturer.

**Film/"Solution" Adhesives - UV-Activateable**

Much work has been put into converting the traditional solution adhesive into
a somewhat "friendlier" system by the use of "reactive solvents". Much of this
has concentrated in producing formulations where the active ingredients,
particularly based on epoxy resin chemistry, have been "dissolved" in blends
of "solvents" such as acrylates and hydroxyacylates. The "solvents" can then
be fixed in the formulation by polymerisation through UV-activation.

The initial energy consumption for mixing/dissolving and for film preparation
will be relatively low but as thermal curing will almost certainly have to
take place, this will add, but not excessively, to the overall energy "bill".

However, to balance this out, the chemistry required for the formulation of
such systems is complex - the acrylates/methacrylates detracting from the
structural properties, ozone will be produced during UV-advancement and, due
to the very low viscosities associated with this class of materials, the
chance of operator contact is likely to be high.

In summary, these are relatively safe systems which, again, throw most of the
onus for personnel and environmental protection on the manufacturer. As the
formulator's knowledge and experience with these chemistries increases, UV­
activation will probably provide a very attractive and relatively "green"
route to structural adhesive formulation and manufacture.

**"Hot-Melt" Thermoplastic Film Adhesives**

When considering structural thermoplastic adhesives, in the context of the
above definition, it is the specialist thermoplastics [eg PES, PEEK, etc]
which readily spring to mind.
The chemistries are very straightforward with, essentially, no associated formulating work. No solvents are used which not only simplifies the equipment used by both manufacturer and end-user but also removes any concerns about operator or environmental contact.

However, by their very nature, these adhesives require very high energy inputs both to manufacture the adhesive and to process it; at these high temperatures, operator contact with the hot (maybe >200°C) melt is a cause for concern.

In summary, this class of adhesives offers several attractions to the end-user but the energy consumption criteria are always likely to restrict their use to specialist applications.

"Hot-Melt" Thermoset Film Adhesives

Under the definition of structural adhesives, given above, it can be argued that this class of materials offers the greatest flexibility and the highest "green" potential.

The fact that these systems are prepared and used by "hot-melt" techniques means that there are no solvents associated with the processes. Further, as most of the raw materials used have very low volatile contents there are very few emission hazards associated with the use and, more importantly, with the curing of these adhesives.

Furthermore, as a wide range of resins, polymers, additives, etc are available to the formulating chemist, the need to use toxic chemicals can be circumnavigated by careful formulation. The replacement of asbestos in structural adhesives is a good example of this.

Much of the above argument will also apply to a formulated paste adhesive. However, the film format readily lends itself to being interleaved with protective foils of polythene and/or release paper, indeed with most film adhesives this is essential to prevent blocking. These protective films will generally stay in place until after the adhesive has been cut to shape and size and is ready to be applied to the substrate; this minimises contact with the operator and the environment.

On applying the adhesive to the substrate, should some degree of tack be required, then either the formulation itself can supply this or a low-temperature "thermal tacking" method can be used; solvent activation is not needed.

As has been indicated above, the film adhesive is cut to size and shape. This leads to less wastage, and hence greater economy, and less resinous material to dispose of.

Finally, controlled flow and glueline thickness can be built into the adhesive system which means that the adhesive stays where it is during cure with less likelihood of molten material coming into contact with the operator.

No system, unfortunately, is free from drawbacks and "hot-melt", thermoset, structural film adhesives are no exception; although in this case they are few.

The very nature of hot-melt mixing and casting coupled with the curing procedures means that these adhesive systems are relatively high energy consumers.

Further, their "packaging" (ie polyethylene and/or release paper interleaving] has to be disposed of once stripped from the adhesive film. Currently this is achieved by incineration or landfill but a more friendly re-cycling process would be of significant advantage.
Conclusions

From the point of view of reducing hazardous exposure of the operator and potential damage to the environment, it has been shown that the manufacture and use of structural film adhesives - particularly those produced by "hot-melt" techniques using thermosetting chemistries - will often offer the safest option to the manufacturer and to the end-user.

The question will always be asked: "Are these 'green' advantages worth the extra cost in energy?" The answer will often be "Yes".