

File No: NA/128

Date: 18/10/93

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION  
AND ASSESSMENT SCHEME**

**FULL PUBLIC REPORT**

**PROBIMER 52 RESIN**

This Assessment has been compiled in accordance with the provisions of *the Industrial Chemicals (Notification and Assessment) Act 1989, as amended* and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by Worksafe Australia which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment, Sport, and Territories and the assessment of public health is conducted by the Department of Health, Housing, Local Government and Community Services.

For the purposes of subsection 78(1) of the Act, copies of this full public report may be inspected by the public at the Library, Worksafe Australia, 92-94 Parramatta Road, Camperdown NSW 2050, between the hours of 10.00 a.m. and 12.00 noon and 2.00 p.m. and 4.00 p.m. each week day except on public holidays.

For Enquiries please contact Ms Tina Anderson at:

*Street Address:* 92 Parramatta Rd Camperdown, NSW 2050, AUSTRALIA

*Postal Address:* GPO Box 58, Sydney 2001, AUSTRALIA

*Telephone:* (61) (02) 565-9466    **FAX (61) (02) 565-9465**

Director

Chemicals Notification and Assessment

**FULL PUBLIC REPORT****PROBIMER 52 RESIN****1. APPLICANT**

Ciba-Geigy Australia Limited, 227-235 Settlement Rd, Thomastown, Victoria.

**2. IDENTITY OF THE CHEMICAL**

Based on the nature of the chemical and the data provided, Probimer 52 resin is considered to be non-hazardous. Therefore, the chemical name, CAS number, molecular and structural formulae have been exempted from publication in the Full Public Report and the Summary Report.

**Other name:** TK 11782 (in the technical reports attached to the notification statement this designation is used for the notified polymer both alone and in a solvent solution; in the present report TK 11782 is used as the designation for the solvent solution)

**Trade name:** The notified polymer is marketed as a solvent solution called Probimer 52M; the polymer itself is referred to as Probimer 52 resin

**Number-average molecular weight:** 3526-5470

**Weight-average molecular weight:** 13500-14000

**Maximum percentage of low molecular weight species (molecular weight < 1000):** 7.1%

**Method of detection and determination:**

IR and NMR spectra

**Spectral data:**

UV/VIS: Major characteristic absorption peaks were (solvent, THF) observed at 209.8, 229.2 and 354.2 nm.

IR: Major characteristic peaks were observed at (KBr pellet) 830, 865, 930, 1036, 1170, 1245, 1380, 1450, 1505, 1540, 1645, 1650, 1660 and 1735  $\text{cm}^{-1}$

NMR: The NMR spectrum was consistent with structure.

**3. PHYSICAL AND CHEMICAL PROPERTIES**

The notified polymer is manufactured in an organic solvent solution and is not normally isolated. However, some physico-chemical properties of the isolated polymer have been determined.

**Appearance at 20°C and 101.3 kPa:** yellow solid

**Glass-transition Temperature:** 86°C

**Density:** 1360  $\text{kg/m}^3$  at 22°C

**Water Solubility:** <0.0001 g/L at 20°C

**Flammability Limits:** Not flammable

**Pyrolysis Products:** Expected to be carbon monoxide, carbon dioxide and hydrogen bromide

**Autoignition Temperature:** >400°C

**Explosive Properties:** Not explosive when subjected to heat, friction or shock

**Reactivity:** The notified chemical is not expected to be oxidising but is expected to be flame retarding. Autopolymerises in light. Is expected to react with amines, amides and anhydrides.

## **Comment on Physical/Chemical Properties**

### **Vapour pressure**

As the notified polymer is supplied in a polymer solution, the vapour pressure of the polymer is not relevant. The high molecular weight of the polymer indicates that its vapour pressure is likely to be low.

### **Hydrolysis**

No indication of hydrolysis has been given by the notifier on the ground that the polymer is insoluble in water. Except for the terminal epoxides, the structure of the notified polymer contains no functional groups which may normally be expected to be susceptible to hydrolysis.

### **Dissociation constant**

The polymer contains no acidic hydrogens or basic groups and dissociation of the polymer is not expected under environmentally relevant conditions.

### **Adsorption/desorption**

OECD G106 requires that the solubility of the test substance be analytically detectable. As this was not the case for the notified polymer adsorption/desorption testing was not required. The polymer is expected to stay with the soil compartment.

## **4. PURITY OF THE CHEMICAL**

**Degree of purity:**     Approx. 98.7%

<b>Chemical name:</b>	2-methoxyethanol
<b>CAS No.:</b>	109-86-4
<b>Weight percentage:</b>	0.7%
<b>Toxic properties:</b>	Worksafe exposure standard of 16 mg/m <sup>3</sup> with an 'Sk' notation (1). In humans, irritation of the eyes, nose and throat; drowsiness, weakness and shaking. Ingestion may be fatal. Prolonged or

repeated exposures may cause headache, drowsiness, fatigue, staggering, personality change and decreased mental ability. Exposed workers have suffered degenerative brain disease and reduced levels of all blood cells. Potential to cause reproductive effects in male and female workers (2).

**Non-hazardous impurities:** (> 1% by weight) None

**Maximum content of residual monomers:** 2.5%

**Additives/Adjuvants:** None

## **5. INDUSTRIAL USE**

Probimer 52 resin is used as a solder mask/protective coating for printed circuit boards. It will be imported as Probimer 52M containing 49% polymer and 51% solvents, these being 1-methoxy-2-propanol and diethylene glycol dimethyl ether. The process has been used at 115 locations world wide since 1975.

The estimated import volume is 1-10 tonnes of Probimer 52M per year for the first year and may rise to a maximum of 20 tonnes per year for the following four years, representing approximately 10 tonnes of the notified polymer per year.

## **6. OCCUPATIONAL EXPOSURE**

The notified polymer will be imported in 20 L steel pails containing 5 kg of the imported formulation to the notifier's warehouse and shipped as required to a single customer's plant. Workers involved in transport and storage of the notified polymer should only come in contact with it in case of an accident in which case spillage should be minimised by the small amount (2.5 kg) of the notified polymer in the containers.

At the customer's plant two mixers add hardener and matting agents directly to the pail containing the notified polymer and the contents are mixed on a paint mixing machine. The pail has been designed to minimise spillage during mixing and the weighing

and mixing is done in a fume cupboard under local exhaust ventilation.

Forty-seven machine and process operators are involved in:

- . pouring the 20 L of mixed epoxy material into a hopper;
- . setting up the machines involved in the entire process;
- . loading cassettes with the printed circuit boards to be coated;
- . preparing the boards and exposing them to UV radiation; and
- . "developing" the exposed circuit boards in solvent prior to baking.

The machine and process operators work in a "clean room", where the air is changed 20 times/hour, positive pressure is maintained, and the temperature and humidity are strictly controlled.

Six technical personnel solve technical problems and seven maintenance personnel repair mechanical breakdowns and malfunctions.

The notified polymer is used in highly controlled conditions, partly because of the need for minimal exposure to the solvents in Probimer 52M and partly because the polymer is photosensitive. Controls in place to reduce exposure to the solvents also serve to minimise exposure to the polymer.

## **7. PUBLIC EXPOSURE**

As the public should not be directly exposed to the notified polymer during manufacture and the coated circuit boards will be used exclusively in telecommunications applications, there is low potential for public exposure.

## 8. ENVIRONMENTAL EXPOSURE

### . **Release**

The polymer is used in the manufacture of printed circuit boards which will be used exclusively in telecommunications applications. Assuming that the export market is developed, the maximum importation volume of Probimer 52 resin is 20 tonne per year. This equates to 9.8 tonnes p.a. of the notified polymer.

The expected total polymer wastage factor resulting from unused residues in the polymer containers, equipment washings, batch residues and spillage has been estimated by the manufacturer at < 0.5% per annum. Potential wastage is minimised since mixing of the formulation occurs directly in the steel shipping pails. In the event of spillage of the formulated product the notifier has indicated that it is to be soaked up in an inert, dry material (sand, vermiculite) for later disposal, with high temperature incineration the preferred method. Notified polymer residues disposed of in this manner should account for < 49 kg p.a.

It has been indicated by the notifier that residues resulting from the curtain coater applicator are collected and returned to the storage hoppers of the curtain coater for reapplication.

The single user of Probimer 52M has indicated that 5 - 10% of the polymer (applied by the curtain coater) will be washed off from the circuit board in a solvent bath after the initial UV curing phase. The gamma-butyrolactone solvent containing the polymer (5 - 10% of applied amount) is currently returned to Ciba Switzerland (via Ciba Thomastown, Victoria) for reprocessing of the solvent. The notifier indicates that it is envisaged that a reprocessing still will be installed at the user's site. If established, a domestic still will require suitable disposal of the reclaimed polymer residues. Residues resulting from the solvent rinsing stage of processing will account for a further 490 - 980 kg p.a. of the notified polymer.

All designated waste polymer will be either self polymerised by UV exposure or mixed with a suitable hardener and thermally cured. In either case, waste polymer will be cured before disposal to landfill. Curing in this manner will result in the formation of a solid polymer matrix.

Probimer 52 resin is intended for use in circuit boards for telecommunications products and, as such, would be expected to be released to the environment when the circuit boards are replaced as a result of component failure or when the telephone itself is disposed of. These wastes will ultimately be consigned to landfill.

#### . **Fate**

Probimer 52 resin is a polymer with very low solubility, therefore leaching from landfill sites is not expected. Incineration of the notified substance is expected to produce oxides of carbon, hydrogen bromide and other possibly toxic gases depending on the conditions of pyrolysis.

The notified polymer is not expected to be released to the environment until it has been fully cured into a solid polymer matrix. The resultant matrix structure should limit the biodegradation of the polymer. Bioaccumulation of the polymer is unlikely due to the high molecular weight (> 1000) of the polymer even before curing.

### 9. **EVALUATION OF TOXICOLOGICAL DATA**

Toxicological data are not required under the *Industrial Chemicals (Notification and Assessment) Act, 1989, as amended* for polymers with a NAMW > 1000. However, data were provided on the induction of mutations in bacteria by the notified polymer. Acute toxicity data also were provided on the formulated product Probimer 52M containing 49% polymer, referred to as TK 11782. These studies are evaluated below.



## 9.1 Acute Toxicity

Table 1 Summary of the acute toxicity of TK 11782

Test	Species	Outcome	Reference
Acute oral toxicity	Rat	LD <sub>50</sub> > 10000 mg/kg	(3)
Acute dermal toxicity	Rat	LD <sub>50</sub> > 3170 mg/kg	(4)
Skin irritation	Rabbit	Slight irritant	(5)
Eye irritation	Rabbit	Non-irritant	(6)
Skin sensitisation	Guinea Pig	Possible sensitiser	(7)

### 9.1.1 Oral Toxicity (Ref No:3)

TK 11782 was diluted in polyethylene glycol (PEG 400) at concentrations of 10, 20 and 50% and administered by gavage at doses of 1000, 2150, 4640, 7750 and 10,000 mg/kg to 5 male and 5 female Tif RAI SPF rats per dose.

Within 2 hours after treatment the rats in all dosage groups showed sedation, dyspnoea, exophthalmus, curved position and ruffled fur. All animals had recovered within 7 to 8 days.

All animals were killed after an observation period of 14 days. No substance-related gross organ changes were observed.

It is concluded that the acute oral toxicity of TK 11782 is > 10000 mg/kg.

### 9.1.2 Dermal Toxicity (Ref No:4)

The backs of 3 male and 3 female Tif RAIf (SPF) rats were shaved 24 hours prior to application of TK 11782 at doses of 2150 and 3170 mg/kg. TK 11782 was evenly dispersed with a syringe and the treatment site was covered with an occlusive dressing which was fastened around the trunk with an adhesive elastic bandage. The dressing was removed after 24 hours and the skin cleansed with lukewarm water.

Within 24 hours after treatment the rats in both dosage groups showed dyspnoea, curved position and ruffled fur. On the fifth day after treatment a slight erythema and oedema were observed. The animals recovered from systemic symptoms within 8 to 12 days.

All animals survived to day 14 after which they were submitted to a necropsy. Despite the lack of control animals, it appeared that no substance-related gross organ changes occurred.

It is concluded that the acute dermal toxicity of TK 11782 is > 3170 mg/kg.

#### **9.1.4 Skin Irritation (Ref No:5)**

The skin irritation potential of TK 11782 was tested in 3 male and 3 female rabbits of the Russian breed.

Two days before treatment the entire back and flank of the rabbits were shaved with an electric clipper and immediately before treatment shaven skin on the left side was slightly abraded.

For treatment, gauze patches were soaked with the test substance and applied to the abraded and non-abraded skin. The patches were covered with an impermeable material and were fastened to the body of the rabbit with adhesive tape. The dressings were removed after 24 hours.

Skin reactions were scored 24 and 72 hours after application of the test substance. No oedema was observed in any rabbit at either time point. Erythema in intact skin varied from very slight (3 rabbits, 24 hours; 2 rabbits, 72 hours) to slight (1 rabbit at both 24 and 72 hours). In abraded skin only very slight erythema was observed in 4 rabbits at 24 hours and 3 rabbits at 72 hours.

It is concluded that TK 11782 is a slight skin irritant.

#### **9.1.5 Eye Irritation (Ref No:6)**

An eye irritation test was performed on 3 male and 3 female rabbits of the Russian breed. TK 11782 in amounts of 0.1 mL was instilled into the left eye of 6 rabbits and the lids were gently held open for one second. The right eye of each rabbit served as

a control. In 3 of the rabbits, about 30 seconds after administration, the treated eyes were flushed with 10 mL of lukewarm water.

No effects on the cornea, iris or conjunctiva of any rabbit was observed at either 1, 2, 3, 4 or 7 days post-treatment.

It is concluded that TK 11782 is not an eye irritant.

#### **9.1.6 Skin Sensitisation (Ref No:7)**

An optimization test (8) was performed using TK 11782 on groups of 10 male and 10 female guinea pigs of the Pirbright strain.

During the induction period the animals received one intracutaneous injection every second day (except weekends) to a total of 10 intracutaneous injections of a freshly prepared 0.1% solution of TK 11782 in propylene glycol. One control group was treated with the vehicle alone.

On the first day, intracutaneous injections of 0.1 mL were administered to the shaven skin of the right flank and back, while on the following days a single intracutaneous injection was given to the back. During the second and third week of the induction period the test material was incorporated in a mixture of the normal vehicle with complete Freund's adjuvant (vehicle:adjuvant::1:1).

Fourteen days after the last sensitising injection a challenge injection of 0.1 mL of a freshly prepared 0.1% solution of TK 11782 in propylene glycol was administered into the skin of the left flank. Ten days after the intracutaneous challenge injection a subirritant dose of the test compound was applied epicutaneously under occlusive dressings which were left in place for 24 hours.

One female in the test group died within 31 days after starting the treatment.

After the intradermal challenge injection, 5/20 animals gave a positive response with the vehicle control and 12/19 animals gave a positive response with TK 11782. This difference is not statistically significant at the 1% level ( $P = 0.018$ ) but is significant at the 5% level.

The results of the challenge dose of TK 11782 applied topically 10 days after the intracutaneous challenge injection were negative. No erythema was observed for 20 animals in the control group or 19 animals in the test group.

It is concluded that, while TK 11782 may be a skin sensitiser, more studies would need to be conducted to prove this conclusively.

### **9.3 Genotoxicity**

#### **9.3.1 Salmonella typhimurium Reverse Mutation Assay (9)**

TK 11782 was assayed for induction of prototrophic back mutants in *Salmonella typhimurium* strains TA 98, TA 100, TA 1535, TA 1537 and TA 1538 and *Escherichia coli* strain WP2 *uvrA* in the presence or absence of metabolic activation provided by rat liver S9 at doses up to 5000 µg/ plate.

Negative controls were within acceptable limits and positive controls (daunorubicin-HCl, 4-nitroquinoline-N-oxide, N-methyl-N'-nitro-N-nitrosoguanidine, 9-aminoacridine-HCl and 2-nitrofluorene without S9; cyclophosphamide and 2-aminoanthracene with S9) gave the expected responses.

Weak positive responses ( $< 10^{-2}$  mutants/ µg) were observed in strains TA 1537 and *E. coli* WP2 *uvrA* at doses of 500, 1000 and 5000 µg/ plate in the absence but not in the presence of rat liver S9. The increases were 2-3 times background and a clear dose-response was observed in *E. coli* WP2 *uvrA*.

It is concluded that TK 11782 may be weakly genotoxic.

### **9.4 Overall Assessment of Toxicological Data**

It is concluded that TK 11782 is of very low acute oral toxicity and low acute dermal toxicity. It is a slight skin irritant but is not an eye irritant. It may be weakly genotoxic and may also be a skin sensitiser. The study on skin sensitisation in guinea pigs was equivocal and the negative result of topical challenge suggests that the skin acts as a barrier to the component of TK 11782 responsible for the positive responses observed after intracutaneous injection.

## **10. ASSESSMENT OF ENVIRONMENTAL EFFECTS**

No aquatic toxicity data were provided, but none are required according to the Act, since the notified polymer has a number average molecular weight (NAMW) > 1000. Due to its high NAMW the polymer is not expected to cross biological membranes and will therefore be of low toxicity.

## **11. ASSESSMENT OF ENVIRONMENTAL HAZARD**

The polymer is unlikely to present a hazard to the environment at any stage of its use. Of the original quantity of polymer imported it is likely that < 10% will be designated waste, resulting from the manufacture and processing of the printed circuit boards. The remainder of the notified polymer will be incorporated into the surface coatings of the circuit boards.

As with the finished surface coating, wastes containing the notified polymer will not be released to the environment until they have been fully cured (by UV/thermal exposure) into a solid polymer matrix. As the matrix so formed is the result of chemical bonding, leaching from landfill is not expected.

The low level environmental exposure of the polymer as a result of normal use indicate that the overall environmental hazard should be negligible.

## **12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS**

The likelihood of adverse effects from short term exposure to Probimer 52 resin either orally, dermally or ocularly is expected to be minimal based on acute toxicity studies.

The results of a skin sensitisation study in guinea pigs were equivocal. A possible positive response was seen following intradermal injection but not following topical application. Also the notified polymer was tested as a solvent solution so that it is possible the observed response was an effect of the solvent. Therefore, the notified polymer may be a weak skin sensitiser. Other results suggest that the notified polymer is a weak genotoxic agent. However, given that the notified polymer is used at only one site under highly controlled conditions, the

risk of adverse health effects may be considered to be low. It is expected that the need to minimise exposure to the solvents in Probimer 52M will also serve to minimise exposure to Probimer 52 resin.

As there is low potential for public exposure to Probimer 52 resin, there should be a minimal risk to public safety.

### **13. RECOMMENDATIONS**

To minimise occupational exposure (and public/environmental if recommendations have been made by these agencies) to Probimer 52 resin the following guidelines and precautions should be observed:

- . if engineering controls and work practices are insufficient to reduce exposure to Probimer 52 resin to a safe level, then personal protective devices which conform to and are used in accordance with Australian Standards (AS) for eye protection (AS 1336, AS 1337) (10,11), impermeable gloves (AS 2161) (12) and protective clothing (AS 3765.1, 3765.2) (13,14) should be worn;
- . good housekeeping and maintenance should be practised. Spillages should be cleaned up promptly with absorbents which should then be put into containers for disposal in accordance with local or State regulations;
- . good personal hygiene should be observed; and
- . a copy of the Material Safety Data Sheet should be easily accessible to employees.

### **14. MATERIAL SAFETY DATA SHEET**

The Material Safety Data Sheet (MSDS) for Probimer 52M containing the notified chemical Probimer 52 resin (Attachment 1) was provided in Worksafe Australia format (15). This MSDS was provided by Ciba-Geigy Australia Limited as part of their notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of Ciba-Geigy Australia Limited.

## 15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), secondary notification of Probimer 52 resin shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

## 16. REFERENCES

1. National Occupational Health and Safety Commission, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment*, Australian Government Publishing Service Publ., Canberra, 1991.
2. *Dangerous Properties of Industrial Materials*, 7th Ed., Sax N. I. and Lewis R. J. Sr Eds, Van Nostrand Reinhold, 1989.
3. *Acute Oral LD<sub>50</sub> of TK 11782 in the Rat*, Data on file, Ciba-Geigy Limited, Basle, Switzerland, Project No. Siss 4551, March 12, 1975.
4. *Acute Dermal LD<sub>50</sub> in the Rat of TK 11782*, Data on file, Ciba-Geigy Limited, Basle, Switzerland, Project No. Siss 4551, May 23, 1975.
5. *Skin Irritation in the Rabbit after Single Application of TK 11782*, Data on file, Ciba-Geigy Limited, Basle, Switzerland, Project No. Siss 4551, May 23, 1975.
6. *Irritation of TK 11782 in the Rabbit Eye*, Data on file, Ciba-Geigy Limited, Basle, Switzerland, Project No. Siss 4551, May 23, 1975.
7. *Skin Sensitising (Contact Allergenic) Effect in Guinea Pigs of TK 11782*, Data on file, Ciba-Geigy Limited, Basle, Switzerland, Project No. 791652, February 4, 1980.
8. Maurer T., Thomann P., Weirich E.G. and Hess R., *The Optimization Test in the Guinea Pig*, Agents and Actions, 5, 174-179, 1975.

9. *Salmonella and Escherichia/ Liver Microsome Test with TK 11782*, Data on file, Ciba-Geigy Limited, Basle, Switzerland, Project No. 791227, March 14, 1980.
10. Australian Standard 1336-1982, *Recommended Practices for Eye Protection in the Industrial Environment*, Standards Association of Australia Publ., Sydney, 1982.
11. Australian Standard 1337-1984, *Eye Protectors for Industrial Applications*, Standards Association of Australia Publ., Sydney, 1984.
12. Australian Standard 2161-1978, *Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves)*, Standards Association of Australia Publ., Sydney, 1978.
13. Australian Standard 3765.1-1990, *Clothing for Protection Against Hazardous Chemicals, Part 1: Protection Against General or Specific Chemicals*, Standards Association of Australia Publ., Sydney, 1990.
14. Australian Standard 3765.2-1990, *Clothing for Protection Against Hazardous Chemicals, Part 2: Limited Protection Against Specific Chemicals*, Standards Association of Australia Publ., Sydney, 1990.
15. National Occupational Health and Safety Commission, *Guidance Note for the Completion of a Material Safety Data Sheet*, 2nd. edition, AGPS, Canberra, 1990.