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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Hexanedioic acid polymer with 1,4-dibutanediamine

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

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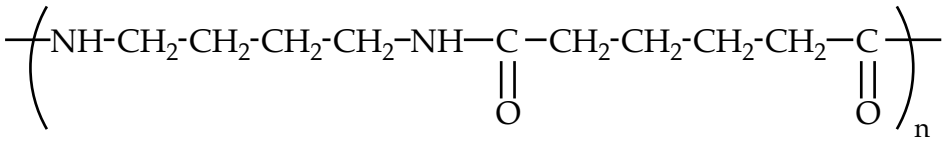
1. APPLICANT

Bribros Pty Ltd of 51-57 Buckhurst Street, SOUTH MELBOURNE VIC 3205 has submitted a notification statement accompanying their application for assessment of a synthetic polymer of low concern, hexanedioic acid polymer with 1,4-dibutanediamine.

2. IDENTITY OF THE POLYMER

Chemical Name:	hexanedioic acid polymer with 1,4-dibutanediamine
Chemical Abstracts Service (CAS) Registry No.:	50327-77-0 (previously listed as 50327-22-5)
Other Name(s):	poly[imino(1,4-dioxo-1,4-butanediyl)imino-1,6-hexanediyl], polyamide 4.6, nylon 4.6
Trade Name(s):	Stanyl
Molecular Formula:	$[NH\text{-}(CH_2)_4\text{-}NH\text{-}C(O)\text{-}(CH_2)_4\text{-}C(O)]_n$, where n = 100

Structural Formula:



Number-Average Molecular Weight:	40 900
Maximum Percentage of Low Molecular Weight Species (Polymers and Oligomers)	
(Molecular Weight < 1 000):	< 1.0%
(Molecular Weight < 500):	< 1.0%

Table 1: Polymer Constituents

Constituent	*CAS No.*	*% Weight*
hexanedioic acid	124-04-9	60
1,4-butanediamine	110-60-1	40

Means of Identification Fourier Transform Infra-red spectrum

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa: smooth hard shiny solid

Melting Point/Glass-transition Temperature: 295°C

Density: 1 180 kg/m^3

Water Solubility: insoluble

Partition Co-efficient (n-octanol/water): not applicable

Hydrolysis as a Function of pH: not applicable until high temperatures (>80°C remains slow)

Flammability Limits: see below

Autoignition Temperature: 420°C

Explosive Properties: spark may cause fines to be explosive in air
(fines to remain < 10 g/m^3)

Reactivity: generally inert, may react with some metallic chlorides and strong oxidising compounds, soluble in strong acids, very polar solvents, and cresol, resorcinol and chloroform.

Particle Size Distribution:
range - µm
extruded cylindrical granules, 2 to 3 mm diameter, minimal fines as supplied but may collect during processing

Comments on Physico-Chemical Properties

Hexanedioic acid polymer with 1,4-dibutanediamine, commercially marketed as Stanyl, is a nylon plastic formed from non-hazardous monomers. Given its extremely high molecular weight and the absence of ionisable groups within the polymer, Stanyl is insoluble in water. The polymer does not contain functional groups that will readily hydrolyse or further react and hence is biologically inert.

Like many plastics, stanyl possesses electrostatic properties which can assist sparking. Fines in air may therefore form explosive mixtures. Stanyl hydrolyses only slowly at higher temperatures in water (> 80°C). Oxidation occurs very slowly, assisted by UV and temperature. Stanyl is marketed for its physical toughness, temperature resistance, and lack of reactivity to be used in physically demanding situations, eg automobile engine accessories.

4. PURITY OF THE CHEMICAL

Table 2: Maximum Weight-Percentage of Residual Monomers

Residual Monomers	*CAS No.*	*% Weight*
hexanedioic acid	124-04-9	0.01
1,4-butanediamine	110-60-1	<0.0005

Table 3: Maximum Weight-Percentage of Impurities

Impurity	*CAS No.*	*% Weight*
pyrrolidine	123-75-1	0.004
pyrroline	109-66-6	0.04
aminobutyronitrile	32754-99-7	0.001

5. USE, VOLUME AND FORMULATION

Hexanedioic acid polymer with 1,4-dibutanediamine will be imported as small granules (2-3mm) combined in several formulations with glass fibres or stainless steel for example, and in polymer mixtures with other plastics, such as polytetrafluoroethylene and polytribromostyrene. A formulation with polytribromostyrene and antimony trioxide (7%) is used in flame retardant grades.

Stanyl is to be remoulded in Australia for automotive and electrical/electronic components, for example:

a) engine - oil filters, chain tensioners, inlet manifolds, and pushrod guides
b) transmission - clutch components, gearbox thrust bearings, and switch housings
c) cooling - radiator end caps
d) electrical - alternator parts, sensors and switches, lighting components
e) brakes ABS controllers
f) circuit board mounted parts

Import volumes are expected to progressively increase from 20 tonnes in the first year to 250 tonnes in the fifth year. At no time is Stanyl expected to be manufactured in Australia.

6. OCCUPATIONAL EXPOSURE

Stanyl will be imported in hermetically sealed bags shrink-wrapped on pallets in containerised shipments with other plastic products. Warehouse personnel will unpack and reload the pallets preserving the hermetic seal to protect the moulding properties of Stanyl, which is hygroscopic. After shipping to the moulding plants, Stanyl will be added to hoppers and fed into high temperature injection moulding systems conventional to the plastics industry.

This process, which involves heating Stanyl to temperatures over 300°C, if not performed in well ventilated surroundings, may expose workers to fumes of toxic chemicals, such as antimony trioxide, which is added to fire retardant grades of Stanyl. Recovery and recycling of unused plastic may involve grinding processes with the possibility of dust and increased fines.

In the first year the notifiers estimate 10 to 20 people at 3 or 4 sites would be involved in handling Stanyl. This number does not include end use workers. Workers involved would include dock, warehouse, transport and plastic moulding workers. As an end product Stanyl will be handled by automotive, electrical and electronic industry workers during assembly and repair. Home repair workers and hobbyists may also be exposed.

7. PUBLIC EXPOSURE

No toxicological data on hexanedioic acid polymer with 1,4-dibutanediamine was supplied. However the high molecular weight, 40 900, of the notified polymer prevents its absorption across biological membranes into tissues. The monomeric constituents of the polymer together are reported to constitute less than 0.02% by weight of Stanyl. The monomers are not hazardous. Other possible contaminants are present at less than 0.05% collectively and are not considered to cause any appreciable exposure.

The notified polymer will not be sold to the public, but plastic articles made from the notified polymer will be made available to the public, resulting in some public exposure. However the notified uses of Stanyl as plastic components in the automobile and electrical industries will limit the nature of that exposure. Ground water contamination as a result of disposal is unlikely because of the low water solubility and the high molecular weight of Stanyl.

Based on the above information, the proposed use of the notified polymer is not considered to pose a significant threat to public health. If the

conditions of use are varied such that greater exposure occurred, further information may be required to assess the hazards to public health.

8. ENVIRONMENTAL EXPOSURE

Release

Release to the environment of the notified polymer as a result of manufacturing is expected to be minimal. The polymer will be fed automatically into moulding machinery from a hopper. Sprue will be reground and reused. Contaminated polymer scraps will be deposited into municipal landfills. Overall, such waste streams would account for between 1% (large production runs) and 5% (small production runs) of the annual throughput (i.e. a maximum of 12.5 tonnes waste polymer to landfill is possible). Used articles containing the polymer will also eventually be deposited in landfills.

Fate

In the case of accidental spillage, pellets of the polymer are expected to remain where they are deposited. Should a spill occur to water, the pellets should settle onto the bottom sediments, where they could be collected. Due to the anticipated negligible solubility of the polymer, leaching from landfill is highly unlikely, and no movement from the landfill site is expected. The majority of the polymer is not expected to be released to the environment until it has been moulded into components. Biodegradation is unlikely. The high molecular weight of the substance also means that bioaccumulation is not likely to occur.
Surface photodegradation of the finished components is expected with sunlight, but this is only likely to occur after the product has been disposed of to landfill, or discarded inappropriately.

9. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were provided which is acceptable for polymers of low concern with a NAMW > 1 000 according to the *Industrial Chemicals (Notification and Assessment) Act.*

10. ASSESSMENT OF ENVIRONMENTAL HAZARD

Disposal of the notified polymer to landfill is unlikely to present a hazard to the environment as it will be in a pellet form or as a finished product. Bioconcentration and leaching are both considered to be unlikely to occur, due to the high molecular weight of the product and its insoluble nature. Biodegradation of the product is also considered unlikely.
The low environmental exposure of the polymer as a result of the proposed

use, together with its expected negligible environmental toxicity, indicate that the overall environmental hazard should be negligible.

11. ASSESSMENT OF OCCUPATIONAL AND PUBLIC HEALTH AND SAFETY EFFECTS

Hexanedioic acid polymer with 1,4-dibutanediamine is a nylon plastic polymer with a molecular weight of 40 900. No reactive or charged groups remain in the notified polymer. The molecular weight and its biological inertness ensure that no significant amount of the polymer will cross biological membranes or be absorbed if ingested or inhaled. The residual monomers, in the notified polymer, are not hazardous and are present at or below 0.01% by weight. Any impurities are also present at extremely low levels, below any significant exposure.

The notified polymer will be imported as a commercial product, Stanyl, in different formulations modified by additives to alter the physical properties for particular uses. Stanyl is packed in hermetically sealed bags containing small granules. Unless there is an accidental spill, workers or the public will not be exposed to the notified polymer during importation and transport. The notified polymer, is not classified as hazardous according to Worksafe Australia criteria.

During processing, Stanyl will be loaded into hoppers and injected at high temperature into mouldings to make end-use products. Heating to over 300°C and machining, including regrinding for sprue recovery and recycling, create the possibilty of occupational exposure via skin, eyes and airways to fumes and dust. Since the polymer itself is capable of carrying an electrostatic charge, fines may form dangerously explosive mixtures in air during processing. Physical irritation to the airways and eyes is also possible due to mechanical irritation. The explosive danger, alone, necessitates minimum levels of Stanyl dust and electrical grounding of possible local charge sources.

Workers involved in the processing of Stanyl, should also be aware that there are health concerns associated with additives used to change its properties as a plastic product. These include flame retardant grades containing up to 7% antimony trioxide. The atmospheric occupational exposure standard for antimony trioxide is 0.5mg/m^3 according to Worksafe, Australia *National Exposure Standards for Atmospheric Contaminants* (1). The International Agency for Research on Cancer(IARC) in 1993 listed antimony trioxide as being possibly carcinogenic to humans (2).

In addition, animal studies, with chronic low exposure to antimony trioxide, have shown increased eye cataracts in rats (3) and clastogenic effects in mice (4). Two studies involving workers exposed to antimony trioxide fumes have shown skin sensitisation or skin reaction including pustules (5,6). These studies in conjunction with current recommended exposure standards would indicate that exposure be kept to a minimum and that monitoring of workplace atmosphere antimony trioxide levels should be conducted wherever the flame retardant grades

of Stanyl are processed. The Material Safety Data Sheets for such products contain suitable warnings to the hazardous nature with respect to antimony trioxide. Flame retardant grades of Stanyl containing more than 1% antimony trioxide are classified as hazardous according to Worksafe Australia criteria with danger of irreversible effects (7).

In its final form toxic components of Stanyl will be locked into the plastic matrix and effectively unavailable to enter the environment. Only at times, of machining and heating during the moulding process, will there be a risk of exposure to fumes and fine dust. Good engineering practice, with exhausting of air born material and adequate ventilation, will limit potential exposure.

The public will come into contact with plastic articles made from the notified polymer, but the physical properties of the polymer will preclude its absorption across biologivcal membranes. Under the conditions of use in the automobile and electrical industries however, significant public exposure to Stanyl products, containing the notified polymer, is considered unlikely. The proposed use of the notified polymer is not considered to pose a significant risk to public health.

12. RECOMMENDATIONS

To minimise occupational exposure to Stanyl, the following guidelines and precautions should be observed:

- It is good work practice to wear industrial clothing which conforms to the specifications detailed in Australian Standard (AS) 2919 (8) and occupational footwear which conforms to Australian and New Zealand Standard (AS/NZS) 2210 (9) to minimise exposure when handling any industrial chemical;

- Good personal hygiene should be practised to minimise the potential for inhalation and ingestion;

- A copy of the relevant MSDS should be easily accessible to employees.

Workers should be aware that some products containing the notified polymer , in particular flame retardant grades, may contain significant levels of antimony trioxide. The Worksafe Australia document *Exposure Standards for Atmospheric Contaminants in the Occupational Environment: Guidance Note and National Exposure Standards* (1) should be used as a guide in the control of workplace exposure to antimony trioxide in these preparations. Appropriate personal protective equipment should be worn where necessary to minimise exposure to this potentially harmful chemical. Workers producing plastic materials from antimony trioxide containing Stanyl should take appropriate precautions to minimise irreversible damage associated with exposure to this possibly carcinogenic compound.

13. MATERIAL SAFETY DATA SHEET

The MSDS for products containing the notified polymer were provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (10).

These MSDS were provided by the notifier as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the notifier.

14. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act secondary notification of Hexanedioic acid polymer with 1,4-dibutanediamine shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

15. REFERENCES

1. National Occupational Health and Safety Commission 1995, 'Adopted National Exposure Standards for Atmospheric Contaminants in the Occupational Environment', [NOHSC:1003(1995)], in *Exposure Standards for Atmospheric Contaminants in the Occupational Environment: Guidance Note and National Exposure Standards*, Australian Government Publishing Service Publ., Canberra.

2. Boffetta P., 1993. Carcinogenicity of trace elements with reference to evaluations made by the International Agency for Research on Cancer. Scandinavian Journal of Work, Environment & Health. 19 Suppl 1 pp 67-70.

3. Newton P.E et al, 1994, ubchronic and chronic inhalation toxicity of antimony trioxide in the rat. Fundamental and Applied Toxicology. 22(4), pp 561-576.

4. Gurnani N., Sharma A. and Talukder G. 1993. Comparison of clastogenic effects of antimony and bismuth as trioxides in mice. Biological Trace Element Research. 37(2) pp 281-292

5. Motolese A. et al. 1993 Contact dermatitis and contact sensitisation among enamellers and decorators in the ceramics industry. 28(2) pp5 9-62.

6. White G.P Jr., Mathias G.G. and Davin J.S. 1993 Dermatitis in workers exposed to antimony in amelting process. J. of Occupational Medicine. 35(4) pp 392-395.

7. National Occupational Health and Safety Commission 1994, *Approved Criteria for Classifying Hazardous Substances* [NOHSC:1008(1994)], Australian Government Publishing Service, Canberra.

8. Standards Australia 1987, *Australian Standard 2919-1987, Industrial Clothing,* Standards Association of Australian Publ., Sydney.

9. Standards Australia/Standards New Zealand 1994, *Australian/New Zealand Standard 2210-1994, Occupational Protective Footwear,* Standards Association of Australia Publ., Sydney, Standards Association of New Zealand Publ, Wellington.

10. National Occupational Health and Safety Commission 1994, *National Code of Practice for the Preparation of Material Safety Data Sheets* [NOHSC:2011(1994)], Australian Government Publishing Service, Canberra.