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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

TDI Polymer in Basonat F DS 3425

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

TDI Polymer in Basonat F DS 3425

1. APPLICANT

BASF Australia Ltd of 500 Princes Highway NOBLE PARK VICTORIA 3174, has submitted a limited notification statement with their application for an assessment certificate for TDI Polymer in Basonat F DS 3425.

2. IDENTITY OF THE CHEMICAL

TDI Polymer in Basonat F DS 3425 is not considered to be hazardous based on the nature of the chemical and the data provided. Therefore the chemical name, CAS number, molecular and structural formulae, molecular weight, spectral data, details of the polymer composition and details of exact import volume and customers have been exempted from publication in the Full Public Report and the Summary Report.

Trade name: Basonat F DS 3425 (contains polymer)

Number-Average Molecular weight: calculated as > 1000

Maximum percentage of low molecular weight species
(molecular weight < 1000): < 50%
(molecular weight < 500): < 10%

Method of detection and determination:
the polymer is identified using Infrared (IR) spectroscopy (Kbr-discs) (spectra provided for polymer and formulation); Gel Permeation Chromatography (GPC) analysis is used to determine molecular weight and weight distribution and Gas Chromatography (GC) was used to determine the content of some of the hazardous impurities; High Performance Liquid Chromatography (HPLC) was used to identify one of the monomeric constituents after derivatization

Comments On Chemical Identity

The polymer is described as a polyfunctional aliphatic isocyanate. It is imported within a solution and is never isolated.

Analysis of the polymer by GPC was provided for identification. The analysis showed a high proportion of low molecular weight material.

3. PHYSICAL AND CHEMICAL PROPERTIES

The notified polymer is imported as an integral component of the formulation, Basonat F DS 3425, and is not isolated from the dispersion at any time, some physical and chemical properties have been determined solely for the formulation and not for the polymer. This is indicated below:

Appearance at 20°C and 101.3 kPa:	clear colourless to yellowish liquid (formulation)
Odour:	aromatic (formulation)
Melting point:	-19°C (formulation)
Density:	1.1 g cm^{-3} at 20°C (formulation)
Vapour pressure:	0.0000006 kPa at 20°C, 0.0003 kPa at 60°C (formulation)
Water solubility:	polymer insoluble, formulation emulsifiable
Fat solubility:	not determined
Partition co-efficient (n-octanol/water) log P_{ow}:	not determined
Hydrolysis as a function of pH:	not determined
Adsorption/desorption:	not determined
Dissociation constant pK_a**:**	not determined
Flash point:	140°C (formulation)
Flammability limits:	not detected
Combustion products:	not stated
Pyrolysis products:	not determined
Decomposition temperature:	not determined
Decomposition products:	not determined
Autoignition temperature:	> 200°C
Explosive properties:	not an explosion hazard

Reactivity/stability: will react with compounds containing -OH and -NH_2 groups

Particle size distribution: not applicable (liquid)

Comments on physico-chemical properties

The notifier states that the polymer is insoluble in water. This has not been defined and seems in doubt as the presence of certain components would tend to increase the solubility. The product, Basonat F DS 3425, is stated to be emulsifiable in water in all proportions at ambient temperature.

The hydrolysis of the polymer has not been determined and would not be expected to hydrolyse as similar chemicals (polyurethanes) do not undergo hydrolysis under the environmental pH range. It should be noted however that the polyfunctional aliphatic isocyanates of the product can undergo hydrolysis to form carbon dioxide and an insoluble product.

Partition coefficient and adsorption/desorption have not been determined due to the claimed low solubility of the polymer.

The notified chemical contains no dissociable hydrogens or basic functionalities.

4. PURITY OF THE CHEMICAL

Degree of purity: > 90%

Toxic or hazardous impurities:

On the basis of the toxic or hazardous impurities and their respective concentrations, listed in the submission, the polymer would not be classified as hazardous. The hazardous impurities considered individually or when in total are in concentrations below that which would require a hazard classification according to Worksafe Australia's *List of Designated Hazardous Substances* (1). The relevant atmospheric exposure standards as listed in Worksafe Australia's *Exposure Standards for Atmospheric Contaminants* (2) for isocyanates should be observed during use of the chemical.

Non-hazardous impurity/ impurities (> 1% by weight): none

Maximum content of residual monomers: < 0.1%

Additives/Adjuvant the formulation, Basonat F DS 3425, contains the notified polymer at a concentration of > 10% as well as the following:

Chemical name: polyfunctional aliphatic isocyanate
Weight percentage: > 60%

The toxic and hazardous impurities in the polymer under consideration and the polyfunctional aliphatic isocyanate in the formulation would result in the formulation being classified as hazardous on the basis of the skin and respiratory sensitisation potential of residual isocyanates. Hexamethylene diisocyanate would be at a maximum level of 1.2%, this exceeds the hazardous threshold resulting in the formulation being classified as hazardous according to the criteria of Worksafe Australia (1). The second polymer in the formulation is the subject of another NICNAS assessment, NA390, and has not been classified as hazardous according to the criteria of Worksafe Australia (1).

5. INDUSTRIAL USE

The formulation, Basonat F DS 3425, a liquid dispersion, containing the notified polymer (> 10% in formulation) will be imported into Australia at a maximum of > 1 tonnes per annum, this will result in a maximum of < 1 tonne per annum of the polymer being imported into the country. The formulation will be imported in either 65 or 230 kg drums and it is most likely that it will be supplied direct to the notifier's customers without repackaging. The formulation will be used as a crosslinking agent (adhesive promoter) for manufacturing laminates. Possible end uses for the adhesive formulations are for laminated films for coating food (eg. food sachets) or for the production of removable protective films. The polymer is to be used in the manufacturing industry only. The notified chemical is currently in use overseas.

6. OCCUPATIONAL EXPOSURE

The polymer dispersion will be supplied direct to BASF's customers. Occupational exposure during transportation and warehousing will be minimal and will only occur due to accidental spillage. Two employees will be involved in unloading the 65 or 230 kg containers at the docks and 1 during warehousing at BASF's facilities at Noble Park, Victoria.

The notifier has not specified customers. There will be approximately 20 employees potentially exposed at three possible customers to the notified chemical during reformulation to manufacture adhesives. At a typical customer's facilities 1-2 operators will unload the drums of the formulation Basonat F DS 3425. Three operators will decant the formulation via pump which will involve exposure for approximately 1 hour/week. The formulation will be used at a concentration of 3-5% to make adhesive. The other components of the adhesive are aqueous acrylic dispersion, polyurethane dispersion and water. In addition other employees will be exposed during maintenance. The notifier estimates that in total 20 employees can come into contact with the notified chemical during reformulation.

In the adhesive products, the formulation Basonat F DS 3425, will be at a concentration of 3-5%, this corresponds to 0.3-0.5% of the notified polymer. The highest level of exposure to the notified chemical will therefore be during addition

and mixing of the Basonat F DS 3425, where employees will be exposed to the polymer at a concentration of > 10%. Basonat F DS 3425 is classified as hazardous and these employees should use the appropriate personnel safety equipment. In addition local exhaust ventilation is employed where natural ventilation is inadequate. In the event of exposure to the formulation, when respiratory protection is not used and ventilation is inadequate, employees can potentially suffer the following symptoms: eye, skin and respiratory tract irritation. Where this occurs over a period of time then skin and inhalation sensitisation can occur.

7. PUBLIC EXPOSURE

There is little potential for public exposure to the notified polymer during storage, transport and formulation into adhesive products. Minor public exposure to the uncured form of the notified chemical may result from accidental spillage during formulation, transport and storage. Spills are to be contained and soaked up with absorbent material such as sand. Disposal of the waste collected in drums is via decontamination with ammonia and/or disposal to landfill or incineration.

The Basonat F DS 3425 dispersion functions as a crosslinking agent (adhesive promotor) and is used at a concentration of 3-5% in the adhesive product and this corresponds to 0.3-0.5% of the notified chemical. The dispersion will be supplied to up to three customers who will formulate adhesive products for an unknown number of customers. These adhesive products will find use only in the manufacturing of protective laminated films and will not be available to the public.

Production losses of the dispersion at each formulation plant are expected to be minimal. Waste washings from cleaning of equipment and residues in containers may enter the sewers, or drum residues may go to landfill at an estimated maximum level of respectively 6 and 10 kg/annum.

The chemical will finally be immobilised as part of a cross-linked and set adhesive which will be bound to packaging films, and there will be significant public contact with the notified chemical in this inert form.

8. ENVIRONMENTAL EXPOSURE

. Release

Release of the polymer under normal conditions of use is claimed to be minimal unless environmental exposure occurs through accidental spillage. Fugitive emissions during transport and use are claimed to be negligible. Customers, at least initially, will be confined to the western suburbs of Melbourne.
Transport and storage will be in 65 kg or 230 kg polyethylene drums. After import the drums will be transported by road directly to the warehouse, from where it will be transported to customers by road.

Release of the polymer to the environment is considered minimal except in the case of a spill. If spillage occurs, during transport or adhesive manufacture, it will be

contained and soaked up with absorbent material such as sand. This waste is placed in properly labelled drums, and removed to an appropriate location for decontamination or disposal to landfill. Decontamination will be by spreading out the waste material on a solid surface and covering with a weak solution of ammonia (4-8% by volume) containing a wetting agent. The material is let stand for 24 hours then collected for disposal either in landfill or by incineration.

The recommended method of disposal of liquid wastes containing materials such as the new polymer is by burning in an approved incinerator. Waste generated at the processing plant from waste washings from mixture vessels is disposed of by treatment in the effluent treatment plant before discharge. The notifier has estimated that less than 6 kg of the new polymer will be discharged for effluent treatment per annum as a result of adhesive manufacture. Empty drums will be decontaminated before being shredded and contained in landfill or being recycled. Waste decontaminant liquor and rinse water are to be treated in the effluent treatment plant.

Release to the environment from the end use in laminated articles is not expected to present any significant hazard. The notifier has estimated that a maximum of 10 kg per annum of the polymer will be disposed of to landfill as residues in empty adhesive containers.

. Fate

Most of the notified polymer is expected to be covalently crosslinked within cured adhesive, which will be bound to the packaging to which it is applied. The final environmental fate of the packaging being either incineration or landfill. A small amount (< 10 kg per annum) of the notified polymer will be disposed of to landfill as residues in used adhesive containers. The inert nature of the cured adhesive means that the polymer is not expected to be mobile within landfill sites.

The small amount of polymer that is released to sewer (< 6 kg per annum) would be expected to partition to the solid sludge, most likely in the form of an insoluble polyurea. The product reacts slowly at the interface with water and liberates carbon dioxide to form an insoluble polyurea with a high melting point. As this polyurea causes blockages etc. in pipelines the product can only be discharged to sewer in low concentrations. The recommended disposal of liquid wastes would be incineration. Any incineration of the notified polymer is expected to produce water and oxides of carbon and nitrogen.

9. EVALUATION OF TOXICOLOGICAL DATA

The Act does not require the provision of toxicological data for polymers of NAMW greater than 1,000. No data are available for the notified chemical and it is therefore not possible to classify the notified polymer on the basis of its toxicological profile.

Analogue toxicity data is available for a compositionally similar material to the formulation, Basonat F DS 3425, which contains the notified polymer. The reports are unsighted (referred to on the Material Safety Data Sheet (MSDS)) and the data is as follows:

Oral LD50 - rat:	> 10000 mg/kg
Eye irritation - rabbit:	irritant
Skin irritation - rabbit	irritant
Acute inhalation - rat	no mortalities after 8 hours exposure in a highly enriched and/or saturated atmosphere at 20^{o}C.

The compositionally similar material has a low oral toxicity and is a skin and eye irritant to the species tested. It was not acutely toxic to rats in a short term inhalation study. However it is likely to cause irritant effects in the respiratory tract. Based on the eye and skin studies and it may cause skin and inhalation sensitisation through chronic exposure on the basis of isocyanate content. On the basis of this information for a compositionally similar formulation and, in the absence of specific toxicological data for the formulation containing the notified chemical, the formulation, Basonat F DS 3425, would be classified as hazardous with the potential for eye and skin irritation.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Ecotoxicological data were not provided, which is acceptable for low volume chemicals (< 1 tonne) according to the Act.

The notifier states that due to the relatively "high" molecular weight of the polymer 1028 it would not be expected to cross biological membranes. However, the notified polymer contains a significant proportion with a molecular weight below 1000 (up to 29% of which 6% has a molecular weight below 500) which could potentially cross biological membranes.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

It is anticipated that the amount of the notified polymer released to the environment will be low. Washings from mixing vessels (< 6 kg per annum) will be discharged into the sewer. Residues in adhesive containers (< 10 kg per annum) and adhesive bound to packaging will be disposed of to landfill or incinerated. The inert nature of the cured adhesive means that the polymer is not expected to be mobile within landfill sites.

The hazard to the environment is restricted by the expected limited release, the low solubility in water of the polymer and its high molecular weight in the cured adhesive film.

The environmental hazard posed by the polymer is rated as low when manufactured into adhesive products as the polymer will be incorporated into the cured adhesive film.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Occupational exposure to the notified polymer will be limited during transport and warehousing and will only occur due to accidental release. Occupational exposure during reformulation and use of formulations containing the notified polymer will be limited due to its low concentration in the imported formulation (>10%) and due to the hazardous nature of the imported formulation. Measures to minimise exposure to the hazardous formulation will also reduce exposure to the notified polymer. The reformulated material, e.g. adhesives will contain only 0.3-0.5% of the notified polymer. As the notified polymer is expected to be covalently crosslinked within the adhesive further occupational exposure will be limited.

The employees with the most likelyexposure to the notified polymer will be those involved in the pumping of the Basonat F DS 3425 and mixing procedures. Exposure will be reduced by the use of appropriate personal safety equipment and local exhaust ventilation, which is employed where natural ventilation is inadequate. In the event of exposure to the formulation, when respiratory protection is not used and ventilation is inadequate, employees can potentially suffer the following symptoms: eye, skin and respiratory tract irritation. Where this occurs over a period of time skin and inhalation sensitisation can potentially occur. It should be noted that these effects result from other components of the formulation rather than the notified chemical. The relevant atmospheric exposure standards as listed in Worksafe Australia's *Exposure Standards for Atmospheric Contaminants* for isocyanates should be observed during use of the chemical.

There is negligible potential for public exposure to the polymer arising from importation, storage, transportation and formulation into adhesive products. Similarly, the potential for public exposure to the chemical during transport and disposal of process waste and clean-up waste after a spill is very minor. There is likely public exposure from the end-use application of the chemical as an adhesive component, but the polymer is present at a very low concentration (< 0.5%) in these adhesives. The chemical will finally be immobilised as part of a cross-linked cured adhesive in laminated films and while there will be significant public contact with the notified chemical in this inert form, there seems no likely route of exposure and absorption.

On the basis of the toxic or hazardous impurities and their respective concentrations, the notified polymer would not be classified as hazardous. The hazardous impurities considered individually or in total, are in concentrations below that which would require a hazard classification according to Worksafe Australia's *List of Designated Hazardous Substances*. The notified substance has a high level of (< 50 and < 10%) of polymers with NAMW < 1000 and < 500 respectively and while no toxic/hazardous impurities exceed the 1% level, there is a significant amount of unreacted isocyanate groups in the polymer preparation. These factors indicate that the formulation may cause skin and inhalation sensitisation following chronic exposure. While the molecular weight of the notified polymer and small reaction products indicate that there is a limited potential for the notified substance to be absorbed across biological membranes into tissues, the Basonat F DS 3425 dispersion crosslinks on contact with water to form an insoluble polyurea with little likelihood of crossing biological

membranes. The formulation containing the notified polymer, Basonat F DS 3425, on the basis of toxicological data, albeit analogue, would be classified as hazardous.

13. RECOMMENDATIONS

To minimise occupational exposure to the TDI Polymer in Basonat F DS 3425 the following guidelines and precautions should be observed:

- If engineering controls and work practices are insufficient to reduce exposure to the TDI Polymer in Basonat F DS 3425 to a safe level, personal protective devices which conform to and are used in accordance with Australian Standards (AS) for eye protection (AS 1336, AS 1337) (4,5), impermeable gloves (AS 2161) (6) and protective clothing (AS 3765.1, 3765.2) (7) and Australian and New Zealand Standard (AS/NZ) footwear (AS/NZS 2210) (8) should be worn;

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

As the notified polymer is only imported as a component of a the formulation, Basonat F DS 3425, which is classified as hazardous, then all of the above listed personnel safety equipment should be utilised when handling this formulation and in addition:

- The workplace exposure standard for isocyanates should be strictly observed.

- The appropriate respiratory device should be selected and used in accordance to AS/NZS 1715 (9) and should comply to AS/NZS 1716 (10).

As the notified chemical is used in a product that comes into contact with food, the notifier should:

- Consult the National Food Authority about requirements under federal food registration.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the formulation, Basonat F DS 3425, containing the notified TDI polymer was provided in a format similar to the Worksafe Australia format (11).

This MSDS was provided by BASF Australia Ltd as part of the notification statement. The accuracy of this information remains the responsibility of BASF Australia Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act, secondary notification of the TDI Polymer in Basonat F DS 3425 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, 1994. *List of designated hazardous substances* [NOHSC:10005(1994)], AGPS, Canberra.

2. American Conference of Government Industrial Hygienists (ACGIH) (1986). *Documentation of the threshold limit values and biological exposure indicies*; 5th edition, 304, 1 (86), ACGIH, Cincinatti, Ohio.

3. National Occupational Health and Safety Commission, 1995. *Exposure standards for atmospheric contaminants in the occupational environment* [NOHSC:3008(1995)], AGPS, Canberra.

4. Australian Standard 1336-1982, *Recommended Practices for Eye Protection in the Industrial Environment*, Standards Association of Australia Publ., Sydney, 1982.

5. Australian Standard 1337-1984. *Eye Protectors for Industrial Applications*, Standards Association of Australia Publ., Sydney, 1984.

6. Australian Standard 2161-1978. *Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves)*, Standards Association of Australia Publ., Sydney, 1978.

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

8. Standards Australia, Standards New Zealand 1994, *Australian/ New Zealand Standard 2210 - 1994 Occupational Protective Footwear, Part 1: Guide to Selection, Care and Use. Part 2: Specifications,* Standards Association of Australia Publ., Sydney, Australia, Standards Association of New Zealand Publ. Wellington, New Zealand.

9. Standards Australia, Standards New Zealand, 1994, *Australian/New Zealand Standard 1715 - 1994 Selection, Use and Maintenance of Respiratory Protective Devices*, Standards Association of Australia Publ., Sydney, Australia, Standards Association of New Zealand Publ., Wellington, New Zealand.

10. Standards Australia/ Standards New Zealand, 1991, *Australian/New Zealand Standard 1716 - 1991 Respiratory Protective Devices,* Standards Association of Australia Publ., Sydney, Australia.

11. National Occupational Health and Safety Commission (1994). *National Code of Practice for the Completion of Material Safety Data Sheets*, [NOHSC:2011(1994)], AGPS, Canberra.