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NATIONAL INDUSTRIAL CHEMICALS
NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

AMMONIUM CARBOXYLATE - CONTAINING FLUOROCHEMICAL URETHANE

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Director
Chemicals Notification and Assessment

Full Public Report

AMMONIUM CARBOXYLATE – CONTAINING FLUOROCHEMICAL URETHANE

1. IMPORTER

3M Australia Pty Ltd, 2-74 Dunheved Circuit, St Marys, New South Wales 2760.

2. IDENTITY OF THE CHEMICAL

Trade names: Ammonium carboxylate-containing fluorochemical urethane; Fluorochemical urethane

Molecular weight: 830-1030

Based on the nature of the chemical and the data provided, ammonium carboxylate-containing fluorochemical urethane is considered to be non-hazardous (1). Therefore, the following details have been exempted from publication: identity of the chemical, composition, methods of determination.

3. Physical and Chemical Properties

Ammonium carboxylate-containing fluorochemical urethane is a reaction product which contains a mixture of different chemicals. At room temperature and atmospheric pressure ammonium carboxylate-containing fluorochemical urethane is a non-volatile, dark yellow to brown waxy solid. Its physical and chemical properties include:

Melting point: 72°C (average)

Boiling point: Decomposes prior to boiling (thermal gravimetric analysis showed a weight loss of 50% at 266°C and 100% at 520°C, probably due to thermal degradation)

Density: 1290 kg/m^3

Vapour pressure: The measured vapour pressure, considered reliable to within an order of magnitude, was 0.0461 Pa at 25°C. Calculation by DASET using the modified Watson correlation (2) returned a value of 1.2×10^{-20} Pa. The higher value obtained by measurement presumably reflects the presence of solvent residues.

Water solubility: 0.9 ppm (column elution method)

Hydrolytic stability: Suspensions of the notified chemical in water, with pH adjusted through addition of ammonia and formic acid, were shaken for 24 h and filtered. The residue from evaporation of the filtrate was dissolved in methyl isobutyl ketone and the resultant solution subjected to fluorine analysis. Total fluorine was 130 ppm at pH 2, increasing to 950 ppm at pH 6 and 1200 ppm at neutral pH and above. While the nature of this residue was not investigated, the results suggest that limited hydrolysis occurs as pH increases, although they may also reflect enhanced solubility of the carboxylates under alkaline conditions.

Partition coefficient: *(n-octanol/water)* log P = 2.7 to 12.3 (12 methanol soluble components were separated and tested by HPLC with reference to non-ionic standards). The ionic nature of the notified chemical (carboxylic acid salts) renders these data unreliable.

Soil adsorption-desorption: Not determined as the chemical is a mixture. In view of the high molecular weight and low water solubility, significant mobility in soils appears unlikely.

Dissociation constant: Not determined because of low water solubility. The notified chemical is comprised of carboxylic acid salts which can be expected to dissociate, particularly under alkaline conditions, similarly to the ammonium salt of 12-hydroxystearic acid.

4. PURITY OF THE CHEMICAL

Degree of Purity: The notifier states that the degree of purity is 95-98%. However, given the levels of fluorinated by-products, the level of purity is probably between 85 to 88%.

Impurities: 12-15%

Note: the impurities represent a mixture of long-chained fatty acids which generally have low acute oral toxicities in test animals but may be mild irritants to the eyes and skin. However, these impurities are unlikely to pose a serious acute health hazard.

5. INDUSTRIAL USES

Ammonium carboxylate-containing fluorochemical urethane is to be imported and used as part of a formulated, water-based product. This formulated product will be applied to hides in the leather tannery industry to enhance the water, oil and stain repellancy of the leather. No reformulation needs to be carried out in Australia.

6. INDUSTRIAL PROCESS AND OCCUPATIONAL EXPOSURE

In the tanning process, the formulated product containing ammonium carboxylate-containing fluorochemical urethane will be applied to the leather in a tumbling drum as the final step in the wet process.

The treated hides will then be supplied to manufacturers and eventually be used in leather apparel, shoe and furniture application. Ammonium carboxylate-containing fluorochemical

urethane is chemically incorporated into the leather and will persist after cleaning.

Skin contact with the notified chemical is highly likely during the tanning process should such processes not be fully mechanised. Given the low vapour pressure of the chemical, excessive exposure to the vapour is usually excluded. However, as a result of heat and agitation (tumbling), a mist which contains the notified chemical and other constituents of the formulated product can be generated in the workplace if the process is not properly enclosed and locally exhausted.

7. PUBLIC EXPOSURE

The formulated product containing ammonium carboxylate-containing fluorochemical urethane will be imported and supplied to the leather industry as a paste and will not be available for public sale. Public exposure to ammonium carboxylate-containing fluorochemical urethane will only be to the formulated product.

In industrial use, the bulk of the product is spent and the residual is eliminated by absorption or precipitation with dissolved solids or waste water sludge. Any remaining product will be partially biodegraded before reaching the waste water treatment system.

Solid waste can be discharged to dumps certified for industrial chemical waste. Unused product either in solution or solid can be incinerated in installations equipped to eliminate halogenated hydrocarbons.

8. ENVIRONMENTAL RELEASE

8.1 Formulation, handling and disposal

Formulation will not take place in Australia and handling will take place entirely within industrial situations. Any spills are likely to be discharged with wastewater (for treatment see below), although appropriate incineration (with scrubbers to remove HF) and controlled discharge are also said to be acceptable means of disposal.

Waste containing the notified chemical will also be generated when treated hides are shaved, trimmed and buffed. Such wastes are likely to be landfilled.

8.2 Use

Ammonium carboxylate-containing fluorochemical urethane will be imported and supplied as an ingredient of a water-based formulated product. This formulated product will be in the form of a paste and will typically be diluted with 40 volumes of water. The diluted product will be incorporated into hides during the wet process after tanning. Based on usage figures supplied by a prospective customer, a typical daily use will be 50 kg of the product (20 kg notified chemical), with an estimated 5% being carried over into wastewater. Initially, the notifier expects tanneries in Victoria to use the product, with additional customers in NSW and Queensland.

9. ENVIRONMENTAL FATE

The main environmental compartment to be exposed to leather protecting chemicals will be the aquatic when spent treatment solution containing unreacted traces of the chemicals is discharged. The company claims that the bulk of the formulated product becomes bound ionically or through hydrogen bonds to the leather during treatment, with an estimated 5% at most (1 kg notified chemical in 2000 L) being carried over into wastewater. This will typically form part of a daily wastewater stream of 0.15 ML (concentration of notified chemical 7 ppm) which will be flocculated before discharge to sewer. The bulk of the residual fluorochemical is expected to become associated with the sludge, which will be dewatered prior to disposal.

Ready biodegradability test results indicate that partial degradation takes place to some extent during wastewater treatment (28 day BOD is 0.263 g/g, or 21% of COD). However, the perfluorinated portions of the molecules can be expected to prove highly persistent in the environment.

The possibility of bioaccumulation in aquatic organisms must be considered because of the high partition coefficients recorded. However, the high molecular weight (above 800) should limit bioavailability, and the carboxylate functionality in the chemical will reduce its lipophilicity (testing revealed a

relatively low fat solubility of 225 ppm for the chemical). Any traces of the chemical that may be absorbed should be readily eliminated.

10. EVALUATION OF TOXICOLOGICAL DATA

10.1 Acute Toxicity

Table 1. Summary of acute toxicity studies with ammonium carboxylate-containing fluorochemical urethane.

Test	Species	Outcome	Ref.
Oral	Rat	LD_{50} > 5000mg/kg	(3)
Dermal	Rabbit	LD_{50} > 2000mg/kg	(4)
Skin irritation	Rabbit	Non irritant	(5)
Eye irritation	Rabbit	Non irritant	(6)
Skin sensitisation	Guinea pig	Non sensitising	(7)

10.1.1 Oral Toxicity (3)

A limit test was carried out in a group of 5 male and 5 female HC/CFY (Remote Sprague-Dawley) rats. Each of the animals was treated with 5000 mg/kg of ammonium carboxylate-containing fluorochemical urethane in 1% aqueous methyl cellulose solution by gavage in a single dose. None of the animals died within 14 days of the treatment. The only sign observed in the animals was pilo-erection, which subsided on Day 3 after administration. Gross necropsy revealed no macroscopic pathological changes. The LD_{50} was greater than 5000 mg/kg for the chemical.

10.1.2 Dermal Toxicity (4)

A limit test was carried out in a group of 5 male and 5 female New Zealand White rabbits. Ammonium carboxylate-containing fluorochemical urethane was applied in a single dose of 2000 mg/kg to the clipped back of each animal and was held in place for 24 hours under a gauze pad moistened with distiled water. At the end of the exposure period, the residual chemical was washed away with warm water. None of the animals died within 14 days of the treatment. The only adverse effect observed in these animals

was slight to well-defined erythema with slight oedema. However, the irritation reaction subsided completely in 5 animals (4 male and 1 female) on Day 3. Gross necropsy revealed no macroscopic pathological changes. The dermal LD_{50} was greater than 2000 mg/kg for the chemical.

10.1.3 **Skin Irritation** (5)

Three New Zealand White rabbits were used in an acute dermal irritation test. Ammonium carboxylate-containing fluorochemical urethane, moistened with distiled water, was applied in a single dose of 0.5 gram to the clipped dorsal skin of each test animal under an occlusive wrap for four hours. At the end of the exposure period, residual chemical was washed away with distiled water. The animals were then examined for signs of erythema, oedema, necrosis and eschar formation at 30 minutes, 2, 3 and 4 days after patch removal. No sign of irritation was observed in all test animals, except that staining of the skin had prevented the assessment of erythema in two test animals.

10.1.4 **Eye Irritation** (6)

Eye irritation was measured by instilling 0.1 gram of ammonium carboxylate-containing fluorochemical urethane into the conjunctival sac of one eye in each of three New Zealand White rabbits. The other eye of each rabbit remained untreated and served as a control. All treated eyes were examined for signs of irritation of the conjunctivae, cornea and iris at 1 hour and 1, 2, 3, 4 and 7 days after the instillation. None of the animals showed any sign of irritation throughout the observation period.

10.1.5 **Skin Sensitisation** (7)

Prior to the induction and sensitisation test, the maximum non-irritant dose was determined in a separate preliminary irritation study. In this preliminary study, 0.5 mL of ammonium carboxylate-containing fluorochemical urethane in acetone, was applied in a single dose to the clipped dorsal skin of each of 4 Hartley/Dunkin Albino guinea-pigs under an occlusive wrap for six hours. At the end of the exposure period, the residual chemical was wiped off. The animals were then examined for signs of erythema and oedema, and again at 24 hours after the application. The maximum non-irritant dose was determined at 40% w/w in acetone, which is also the saturation concentration.

Following the determination of the maximum non-irritant dose, a Buehler test was undertaken. The test group and control group each contained 10 Hartley/Dunkin Albino guinea-pigs. In this induction and challenge study, the same dose and application procedures were used (as described above) and repeated weekly for three weeks in the 10 test animals. Two weeks after the last induction exposure, a single dose of the test chemical was applied to each of the 10 test and 10 control animals in the same application procedures but at different sites on the back of the animals. The animals were examined for signs of erythema and oedema at 24, 48 and 72 hours after the challenge exposure. No sign of irritation was observed in any of the irritation control or induction and challenge groups of animals. These results indicate that ammonium carboxylate-containing fluorochemical urethane is a non-sensitiser in guinea-pigs.

10.2 Short-term Repeated Dose Study

10.2.1 28-Day Dermal Toxicity (8)

A test group and a control group each containing 10 New Zealand White rabbits (5 male and 5 female) were used in this study. A daily dose of 1000 mg/kg of ammonium carboxylate-containing fluorochemical urethane as 50% w/v suspension in 1% aqueous methyl cellulose (that is, 2 mL/kg/day) was applied to the clipped dorsal skin of each test animal under an occlusive wrap for six hours for 28 consecutive days. Animals in the control group were treated similarly but only with the vehicle, 1% aqueous methylcellulose. The animals were examined twice daily for signs of toxicity, ill health and behavioural changes.

No clinical signs of toxicity or mortality were observed in all the animals. Slight dermal erythema and occasional slight oedema were observed in most of the test and control animals during the study. Gross necropsy revealed no treatment-related macroscopic pathological changes. A small but statistically significant ($p < 0.05$) increase in serum albumin level was found in the test animals. No other haematological and biochemical abnormalities were observed, which could be attributed to the administration of the test material.

10.3 Genotoxicity

10.3.1 Ames Test (9)

Ammonium carboxylate-containing fluorochemical urethane was tested for mutagenicity in the Ames *Salmonella*/microsome assay using *Salmonella typhimurium* strains TA1535, TA1537, TA1538, TA98 and TA100, both in the presence and absence of an exogenous mammalian metabolic activation system (Aroclor 1254 induced S-9). The dose levels used in the test ranged from 10 - 5000 ug per plate and the mutation assays were conducted using 3 plates at each dose level. Tests were performed twice. Positive control tests were also performed (2-anthramine for all test strains; sodium azide for TA1535 and TA100; 9-aminoacridine for TA1537; and 2-nitrofluorene for TA1538 and TA98).

An increase in the number of revertant colonies per plate was not observed in any of the five strains both in the presence and absence of an exogenous mammalian activation system. Significant increases were only observed in the positive controls. These results indicate that under the test conditions, ammonium carboxylate-containing fluorochemical urethane was not genotoxic in *Salmonella typhimurium*.

10.3.2 Mouse Micronucleus Test (10)

Ammonium carboxylate-containing fluorochemical urethane in 1% aqueous methylcellulose was administered by gavage to a total of 60 CD-1 Swiss mice (15 animals/sex/group) at a dose of 0 or 8000 mg/kg. An additional 5 animals/sex was treated with 4 mg/kg mitomycin C by intraperitoneal injection and served as the positive control group. Bone marrow smears were obtained from the test group and negative control animals at 24, 48 or 72 hours after the treatment.

No significant increase in the frequency of micronucleated polychromatic erythrocytes was observed in the test animals. A slight but statistically significant reduction in the ratio of polychromatic to normochromatic erythrocytes was detected only in test animals at the 48 hours sampling time. In the positive control group, highly significant increases in the frequency of micronucleated polychromatic erythrocytes were observed. These results indicated that under the test conditions, the test chemical did not produce micronuclei in the polychromatic erythrocytes in the test species.

10.4 Overall Assessment of Toxicological Data

Ammonium carboxylate-containing fluorochemical urethane exhibited very low acute oral and dermal toxicities in test animals (oral LD_{50} > 5000 mg/kg in rats and dermal LD_{50} > 2000 mg/kg in rabbits). The chemical is not irritating to the eyes and skin, and does not cause skin sensitisation. A 28-day animal study indicates that it has also a very low repeated dose toxicity by the dermal route.

The chemical was not genotoxic in an Ames test or a mouse micronucleus test.

11. ASSESSMENT OF OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Exposure to ammonium carboxylate-containing fluorochemical urethane in the tanning process can be significant through direct skin contact and inhalation, if proper control measures are not implemented. However, given the very low oral and dermal toxicities observed in test animals and its non-irritating and non-sensitising properties, exposure to the chemical alone should not pose a significant acute occupational health and safety hazard to workers.

12. ASSESSMENT OF MATERIAL SAFETY DATA SHEET

The Material Safety Data Sheet (MSDS) for ammonium carboxylate-containing fluorochemical urethane is provided at Attachment 1. This MSDS was supplied by 3M Australia Pty Ltd as part of their notification statement. The accuracy of this information remains the responsibility of 3M Australia Pty Ltd.

13. ASSESSMENT OF PUBLIC HEALTH EFFECTS

The potential for public exposure to ammonium carboxylate containing fluorochemical urethane is expected to be minimal, providing that good manufacturing processes are adhered to and waste material is disposed of in the approved manner.

Given the apparent lack of acute toxicity shown by the material, there appears to be negligible risk from accidental spillage during transport.

14. ENVIRONMENTAL EFFECTS

The toxicity of ammonium carboxylate-containing fluorochemical urethane to fish (fathead minnow) and aquatic invertebrates *(Daphnia magna)* was obtained under static conditions using nominal concentrations. In each case, no mortalities were recorded at the highest concentration tested (1000 ppm) when the substrate was added directly as a solid, but note that this greatly exceeds the water solubility and the exact concentration to which the fish were exposed is unclear. The toxicity to fish increased when butyl carbitol was used as carrier (96 h LC_{50} = 100-500 ppm), but remained in the practically nontoxic range. These results must be viewed cautiously because nominal test concentrations greatly exceed the solubility, but indicate that adverse effects are unlikely under environmental conditions.

15. ENVIRONMENTAL HAZARD

The aquatic environment will be exposed to the leather protecting chemicals when unfixed residues are discharged with wastewater. However, as noted above, estimated concentrations of the notified chemical in tannery wastewater are in the order of 7 ppm and will be reduced further when waste water is flocculated and desludged, and during subsequent sewage treatment. For example, wastes which pass through the Werribee Treatment Complex will form part of a daily waste stream of 500 ML, or a greater than 3000 fold dilution of tannery effluent (*ie* from 7 ppm to around 2ppb). Predicted environmental concentrations following dilution by receiving waters would be expected to be in the sub-ppb range. The predicted environmental hazard is low as the chemical does not appear to have significant bioaccumulation potential and displayed minimal aquatic toxicity and some tendency to biodegrade in standard tests.

16. RECOMMENDATIONS FOR THE CONTROL OF WORKER EXPOSURE

In work situations where there is worker exposure only to ammonium carboxylate-containing fluorochemical urethane, or where

there is exposure to other substances which are not significantly more hazardous than ammonium carboxylate-containing fluorochemical urethane, the following guidelines and procedures should be observed:

. the work process should be carried out in a well-ventilated area;

. a copy of the MSDS for the notified chemical should be made available to all personnel who may have exposure to the chemical; and

. appropriate impervious gloves (for example, rubber or PVC gloves) should be worn to prevent prolonged skin contact with the chemical.

17. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), secondary notification shall be required by 3M Australia Pty Ltd if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

18. REFERENCES

(1) National Occupational Health and Safety Commission, *Guidance Note for Determining and Classifying a Hazardous Substance*, In Press, 1991

(2) Grain CF, Vapor Pressure, in Lyman WJ, Reehl WF and Rosenblatt DH, *Handbook of Chemical Property Estimation Methods*, McGraw-Hill, 1982.

(3) Acute Oral Toxicity to Rats of T-3599, Data on File, 3M Australia Pty Ltd, Report No. 84870D/MIN11/AC, 1985

(4) Acute Dermal Toxicity to Rabbits of T-3599, Data on File, 3M Australia Pty Ltd, Report No. 84864D/MIN12/AC, 1984

(5) Irritant Effects on Rabbit Skin of T-3599, Data on File, 3M Australia Pty Ltd, Report No. 84751D/M16/SE, 1984

(6) Irritant Effects on the Rabbit Eye of T-3599, Data on File, 3M Australia Pty Ltd, Report No.84750D/MIN15/SE(G), 1984

(7) Delayed Contact Hypersensitivity in the Guinea-Pig with T-3599, Data on File, 3M Australia Pty Ltd, Report No. 8539D/MIN13/SS, 1985

(8) The Effects of Repeated Dermal Application of T-3599 to Rabbits for Twenty-Eight Days, Data on File, 3M Australia Pty Ltd, Report No. M17/85282, 1985

(9) In Vitro Microbiological Mutagenicity Assays of 3M Company's Compound T-3599, Data on File, 3M Australia Pty Ltd, Report No. LSC-3145, 1984

(10) Micronucleus Test on T-3599, Data on File, 3M Australia Pty Ltd, Report No. MIN14/84914, 1984